Hazardous and Industrial Solid Waste Testing and Disposal

Sixth Volume

Lorenzen/Conway/Jackson/
Hamza/Perket/Lacy
editors

ASTM STP 933

HAZARDOUS AND INDUSTRIAL SOLID WASTE TESTING AND DISPOSAL: SIXTH VOLUME

ASTM SPECIAL TECHNICAL PUBLICATION 933

Douglas Lorenzen, Pennsylvania Department of Environmental Resources, Richard A. Conway, Union Carbide Corporation, Larry P. Jackson, Western Research Institute, Ahmed Hamza, Alexandria University, Cary L. Perket, Environmental Engineering and Management, Ltd., and William J. Lacy, U.S. Environmental Protection Agency, editors

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Foreword

This publication, *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume*, contains papers presented at two symposia: the Third International Symposium on Industrial and Hazardous Waste presented at Alexandria, Egypt, 24–27 June 1985, and the Symposium on Environmental Test Method Development presented at Colorado Springs, CO, 8–9 May 1985.

The Third International Symposium was sponsored by Alexandria University, ASTM Committee D-34 on Waste Disposal, the U.S. Environmental Protection Agency, the U.S. Agency for International Development, and the United Nations Economic Commission for Western Asia. Richard A. Conway, Union Carbide Corporation, Ahmed Hamza, Alexandria University, and William Lacy, U.S. Environmental Protection Agency, served as chairmen of the symposium and are editors of the resulting publication.

The Symposium on Environmental Test Method Development was sponsored by ASTM Committee D-34 on Waste Disposal. Douglas Lorenzen, Pennsylvania Department of Environmental Resources, and Cary L. Perket, Environmental Engineering and Management Limited, served as chairmen of the symposium and are editors of the resulting publication.

Larry P. Jackson, Western Research Institute, also served as editor of this publication.

A Note of Appreciation to Reviewers

The quality of the papers that appear in this publication reflects not only the obvious efforts of the authors but also the unheralded, though essential, work of the reviewers. On behalf of ASTM we acknowledge with appreciation their dedication to high professional standards and their sacrifice of time and effort.

ASTM Committee on Publications

Related ASTM Publications

Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing (Fifth Volume), STP 925 (1986), 04-925000-16

Hazardous and Industrial Solid Waste Testing: Fourth Symposium, STP 886 (1986), 04-886000-16

Hazardous and Industrial Waste Management and Testing: Third Symposium, STP 851 (1984), 04-851000-16

Hazardous and Industrial Solid Waste Testing: Second Symposium, STP 803 (1983), 04-805000-16

Hazardous Solid Waste Testing: First Conference, STP 760 (1982), 04-760000-16

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Introduction

The need for improved test methods relating to disposal, treatment, and characterization of hazardous and industrial solid wastes continues, despite considerable progress since the first ASTM symposium on this subject in 1981. Methods are required to

- Characterize and analyze solid wastes in terms of potential hazards and factors that affect selection of treatment and disposal options.
- Evaluate treatment and disposal processes and operations in terms of efficacy in accomplishing the intended result.
- Assess existing sites to ascertain the need for corrective action and point to alternatives for such action.

This Special Technical Publication (STP) is the sixth volume of test methods developed by ASTM toward fulfilling the above needs. The other ASTM STPs on solid waste testing containing papers from other symposia are listed below, along with locations and the dates of the symposia.

STP 760: Fort Lauderdale, Florida, 14–15 Jan. 1981.
STP 805: Lake Buena Vista, Florida, 28–29 Jan. 1982.
STP 851: Philadelphia, Pennsylvania, 7–10 March 1983.
STP 886: Arlington, Virginia, 2–4 May 1984.
STP 925: New Orleans, Louisiana, 8–9 May 1986.

Test methods for this publication were selected from two ASTM symposia held in 1985, one in Alexandria, Egypt, and one in Colorado Springs. About one-third of the presented papers were selected; they underwent peer review and often extensive revision before publication.

ASTM Committee D-34 on Waste Disposal sponsors a symposium each year on "Industrial and Hazardous Wastes." Usually, every other year, ASTM opens this symposium to papers from the international scientific community and alternates the location of these international symposia between the United States and various other host countries. Committee D-34's Third International Symposium was held 24 through 27 June 1985, in Alexandria, Egypt. It was cosponsored by Alexandria University and the U.S. Environmental Protection Agency.

At this international symposium, 104 papers were presented, and it was attended by over 350 experts from 35 countries. This volume contains 25 of the papers that deal with solid waste issues. Twenty-five other papers dealing

with liquid waste treatment were published by the United Nations Economic and Social Commission for Western Asia in a publication entitled *Management of Industrial and Hazardous Waste*, dated Dec. 1985.

Nine papers presented at a D-34 "mini-symposium" in Colorado Springs, 8 and 9 May 1985, entitled "ASTM Environmental Test Method Development" are also contained in this volume. These papers concern the work of Committee D-34 in developing test methods and specifications for environmental monitoring and waste analyses.

It is the objective of these symposia to stimulate research and provide a forum for the exchange of new information and ideas on the management of hazardous and industrial waste. The Alexandria symposium was no exception and, in fact, provided some of the most relevant work to have been exchanged in an international forum in many years. The papers selected for publication covered seven different subject areas: (1) contaminant and leaching assessments, (2) ground water and contaminant migration assessments, (3) incineration of hazardous waste, (4) liner assessments, (5) site monitoring and assessments, (6) waste testing, (7) waste treatment alternatives. ASTM test method development papers came from the Colorado Springs symposium.

For the various papers presented, it is interesting to note differences apparent in the environmental research effort and environmental direction of developing and developed countries. The major emphasis in developed countries has switched from treatment of gaseous emissions, water, and wastewater to treatment and disposal of solid wastes and remediation of waste disposal areas. Developing countries, on the other hand, seem to be placing more emphasis on municipal wastewater and advanced industrial wastewater treatment processes. This is not to say that either group does not or is not striving to make improvements in all areas.

This progression can be traced in the United States from the post-war era of the 1940s, 50s, and 60s, in which a large industrial growth took place to meet the demands of a country emerging from a depression and world war. People were demanding more consumer goods, and little attention was being given to protecting the environment. By the end of the 1960s, the United States was experiencing a very high standard of living, and the people were realizing that the life they were working so hard to improve was at the same time suffering from significant environmental neglect. This awareness gave rise to Earth Days in the late 1960s and a push for environmental laws and regulations. These laws and regulations were focused on controlling and improving air emissions and water discharges. There was a large push for more research in these areas, and many significant technological advances were made.

From this point, it was a logical progression to the development of hazardous waste control. Improvements in air and water treatment technologies

brought about increased industrial solid waste disposal problems. Industrial treatment sludges, along with an array of other industrial and hazardous wastes, were being indiscriminately dumped and subsequently leached back into the environment through poor and improper disposal practices. The public's fear over this situation was heightened by the well publicized problems at such places as Love Canal, Valley of the Drums, and Lipari Landfill.

In response to this environmental contamination and the massive citizen unrest, fear, and outcry over these revelations, EPA issued one of the most comprehensive and technically complex set of regulations related to solid wastes ever promulgated. States soon followed with similar regulation packages that were in many cases even more comprehensive and inclusive than the federal regulations.

Today, as a consequence of these regulations, there is a very serious shortage of disposal sites throughout the United States. The single, clearest, most often expressed citizen view on waste management is that we must find alternatives to landfills. Industry is responding with improved waste management practices, substituting hazardous substances used with less toxic ones, better in-plant control of production lines to reduce waste volume, recycling, reclaiming, and reusing many wastes previously discarded, and by improving methods for treatment and detoxifying wastes. Although there is a long way to go, significant strides have been made by industry and government in meeting this challenge.

Many developing countries have also realized the importance of maintaining the integrity of our environment as evidenced by a sincere interest in information exchanges such as international symposia, the research in progress, and by their information of environmental commissions, ministries, and other governmental agencies. It is possible that these developing countries will undergo the same sort of metamorphosis that developed countries are now experiencing as the people realize how real a threat industrial expansion without adequate environmental controls can be to a nation's health, environment, and future.

Industrial expansion is essential to both developing and developed countries to compete or maintain their place in the world markets and improve their standard of living. With world-wide industrial expansion comes not only intra-country environmental stress but intercountry and global stress as well. To solve this very real world-wide threat, all countries must work together in controlling waste generation, treatment, and disposal. International commissions should be organized to ensure appropriate standards among all nations and to encourage and pressure those who are reluctant to respond.

Committee D-34 thanks Alexandria University, the Egyptian Government, and all participants in the Third International Symposium on Industrial Hazardous Waste for furthering this cause for international cooperation in solving this very complex and important issue.

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Contaminant and Leaching Assessments

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Leaching Test Characterization of Iron and Steel Industry Waste

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REFERENCE: Philipp, J. A., Endell, R., Raguin, J., and Dechelette, O., **"Leaching Test Characterization of Iron and Steel Industry Waste,"** *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 7–27.

ABSTRACT: The iron and steel industry generates considerable tonnages of solid waste, and although much of it is to a large extent valorized, some 50 kg of waste to every tonne (1000 kg) of steel have to be discharged or disposed of as waste. A good environmental protection policy calls for a ban on dumping of special waste materials, which there are strong grounds for fearing may be of a toxic and dangerous nature. Except in specific cases, it is difficult to tell from the composition of a waste material whether or not it is of a "special" nature. Characterization simulations have to be made to ascertain the extent to which the waste material can release harmful elements, such as heavy metals, when in contact with rainwater and in some cases other waste materials. Such is the object of the leaching tests, which have or are being developed in many countries at the instigation of the authorities and industrialists: Federal Republic of Germany, South Africa, Australia, France, Great Britain, Italy, Japan, the United States, and so forth. The International Iron and Steel Institute (IISI) has, within its Environment Committee, made a comparison of the resultats obtained with different national tests using the same specimens.

KEY WORDS: hazardous wastes, chemical analysis, toxicity, data comparison, landfill disposal, International Iron and Steel Institute leaching-test procedures

General

Iron and Steel Industry Waste

Iron and steel production plants generate considerable tonnages of solid or sludge waste: on average around 500 kg per tonne (1000 kg) of steel for all types combined [*1,2*]. As shown in Fig. 1, most iron and steel waste, 94% in

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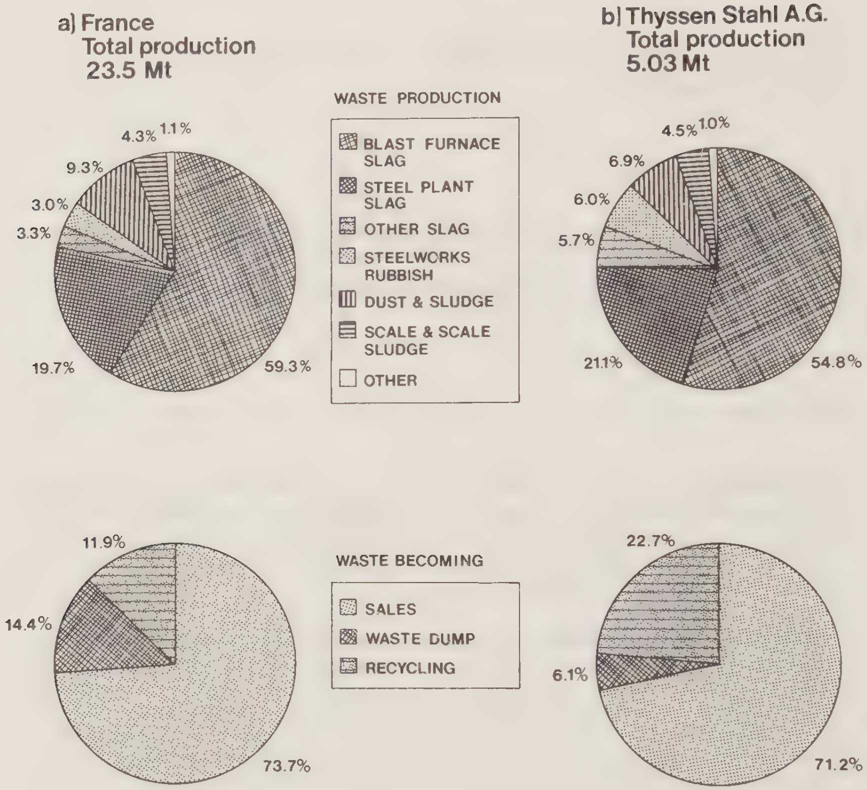

FIG. 1—*Production of specific waste and by materials* (a) *for the French Steel industry in 1974 and* (b) *for a German steel plant in the business year, 1981/1982* [3].

the case of Thyssen [*3*] in 1981, 88% for the French iron and steel industry as a whole in 1974, is valorized, either through internal recycling, or reuse in other industries: road building and cement-making, in particular for blast furnace slag [*4*], production of fertilizers for oxygen steel mill slag, and nonferrous metals industry for dust and sludge [5]. This means that only a very low proportion of the wastes generated are actually dumped, in the order of 50 kg for every tonne (1000 kg) of steel. These essentially include steel plant slag of no agricultural value, nonrecyclable refractory waste, dust and sludge, and very fine scales.

Administrative Constraints on Waste Disposal

In most industrialized countries, increasingly stricter administrative controls are being enforced to ensure that the disposal of industrial wastes is not detrimental to the environment. The 15 July 1975 Directive, for instance,

published by council of the European Economic Community provides that "member states take the necessary measures to ensure that waste materials are disposed of without endangering human health or the environment." Wastes must therefore be disposed of in such a way that the receiving site not be endangered either of the nature of the waste or of the site itself (nature of the soil and subsoil, hydrogeology, and permeability).

Case of Special Waste Materials

In all countries, particular attention is focussed on special wastes, that is to say, in European Economic Community terminology (Council directive of 20 March 1978) to "wastes containing officially listed substances or materials of a nature, quantity or concentration such that they constitute a risk factor for health or the environment." The list published by the Council of Europe refers in particular to cadmium, hexavalent chromium, lead, and selenium compounds. National laws can cover other elements, for example, arsenic, copper, fluorine, mercury, nickel, vanadium, zinc, and so forth.

Regulations generally assess the pollutant nature of a waste material on the basis of two types of criteria that vary from one country to the next, and according to the elements requiring special attention:

- either according to its composition, such is the case in Holland, a country where water and soil pollution can have particularly devastating effects. The same applies in Japan for certain waste materials to be backfilled into the sea such is also the case in France with the thresholds proposed for two elements: chrome VI (100 mg/kg) and vanadium (1000 mg/kg) or
- according to the results of a national accelerated leaching test in an aqueous medium, such is the case in France, Great Britain, Japan, and the United States.

The choice of leaching tests is due to the fact that the major risk of pollution with deposited waste is that pollutant elements can be carried away by water which plays a twofold role: first, it provides a physical, chemical and microbiological medium in which waste can interact with other wastes, and second, it serves to propagate in the subterranean environment pollutant elements generated by the waste. Leaching tests are also needed insofar as at present there exists no model of the evolution of waste materials deposited in a slag heap or tip or of the propagation of the pollution caused as a result.

Theme of the Report

There can be no question of an industrialist taking the slightest risk, particularly in respect of his fellow man, when disposing of waste materials. For him, having a reliable test and realistic standards to go by is therefore an absolute necessity. On the other hand, the disposal of wastes regarded as

toxic and dangerous is very costly because administrative standards are very stringent. One consequently has to be certain of the validity of the selection criteria being applied.

To provide the industry with objective response factors, the International Iron and Steel Institute (IISI) conducted a survey among members of its Environment Committee, including a comparative study between several countries of a few representative specimens of the main waste materials deposited. This comparison has been complemented by national studies, in particular those made in France and Great Britain [*6*].

Leaching Tests Adopted

There are a great many leaching tests being used the world over. Surveys have been done on the subject, and we would mention in particular the one conducted in 1977 by the ASTM covering 14 laboratories [*7*] and the summary work recently done by Colin [*8*] in France. Colin recorded a total of 30 tests: 11 officially recognized or prescribed by official bodies and 19 mentioned and described in technical literature. Tests fall into two main categories, tests with mechanical stirring of waste and water, tests with percolation in a water column through the waste material; the 11 official tests come under the first category. The IISI, for its part, concentrated its survey on the methods in use in eight countries, be they official or professional. These include the characterization methods used in West Germany, France, Japan, and the United States, as well as those applied in iron and steel plants or research centers in South Africa, Australia, Great Britain, and Italy.

West Germany

The official procedure according to standard on Sludge and Sediments: Determination of the Leachability of Water S4 (DIN 38414) provides that leaching be done by mixing and stirring waste with pure water. In some cases leaching is either a single-stage 24-h operation only, or involves several successive stages. The German standard distinguishes, as do other national standards (for example, in France) three categories of leachable elements:

(1) elements that are easily dissolved or present in waste in such small quantities that eluting need only be done once,
(2) elements that are not so easy to dissolve or are present in waste in such great quantity that leaching must be done in several stages, and
(3) elements whose behavior alters during the study.

There are at present no official texts in Germany allowing for a classification of waste materials to be made according to leaching test results. A draft is however being drawn up.

France

The French Ministry for the Environment has proposed a protocol on the extraction of soluble substances contained in solid or pasty waste [9]. According to this protocol, soluble or removable compounds are extracted by mechanical stirring until constant physico-chemical parameters are achieved (pH, resistivity, degree of oxidation). A second and then a third extraction are done to check the level of solubility or elutriability of leachable substances. Mechanical stirring using a shaker sets the liquid and waste in motion one against the other. The liquid used is distilled or demineralized water which saturated in carbon dioxide (CO_2) and then air, at a temperature of between 18 and 25°C, has a resistivity of between 0.2 and 0.4 MΩ and a pH of around 4.5. The waste is homogenized (with separation of the liquid phase if necessary) and then ground to pass a 4-mm sieve. This test, called the "INSA test" after the laboratory, Institut National des Sciences Appliquées, which developed it, is done using a polyethylene jar with a capacity of 2 L or more, into which 100 g of waste and 1 L of water are placed.

The parameter retained for the most elements is the total quantity of leachable matter (LM) extracted during the three successive extractions and calculated as follow

$$\text{LM (mg/kg)} = 10 \times (a_1 + a_2 + a_3)$$

where a_i is the concentration of element "a" in the ith extraction leachate ($i = 1, 2, 3$).

The values obtained are then compared with the proposed thresholds (Table 1), which have not yet been officially published.

Japan

The Japanese law of 17 Feb. 1973 specifies the methods to be used for leaching and interpreting the results obtained. The Japanese test uses 50 g of waste and 500 mL of deionized water. Mixing is done in a container placed horizontally and rotated by means of rollers.

Toxicity thresholds vary according to whether wastes are to be deposited on a slag heap (Table 1) or, the most severe case, used as seafill material.

United States

In the test promulgated by the U.S. Environmental Protection Agency (EPA) [*10*] on 19 May 1980, the waste is first separated into its liquid and solid components by filtration using a 0.45-μm pressure filter. The solid phase that results is then leached, after grinding to pass a 9.5-mm sieve, using deionized water acidified to pH 5 with 0.5 N acetic acid, and this pH value

TABLE 1—*Classification of hazardous wastes by leaching tests. Toxicity thresholds used for the national standards in the United States and Japan and for the draft standard in France.*

	United States	Japan[a]	France[b]
Heavy Metals	Leachate Concentrations, mg/L		Leachable Matter, mg/kg
Ag	5	...	...
As	5	1.5	100*
Ba	100	...	1000
Cd	1	0.3	100
Cr total	5	...	1000
Cr VI	...	1.5	100*
Hg	0.2	0.005	100*
Pb	5	3	1000
Se	1	...	100*
Zn	...	...	5000

[a]Reglementation for landfill disposal.
[b]Total quantity leached during the three extractions or initial concentration in the waste (asterisks).

must, if possible, be maintained throughout the operation. Waste and water are mixed in a proportion of 1 to 16. The mixture is agitated by stirring or end-over rotation for 24 h. Once extracted, the leachate is diluted by adding a volume of water V determined as follows

$$V\,(\text{ml}) = 20\,W - 16\,W - A$$

where

W = initial weight of sample, g and
A = quantity of 0.5 N acetic added, mL.

The leachate is separated from the waste, using a 0.45-μm filter, and it is combined with the initial liquid derived from the waste. The combined liquid is then analyzed and the results obtained and expressed in milligrams per litre (mg/L) are compared with the thresholds shown in the Table 1. Wastes with extracts exceeding these thresholds are deemed to require special handling.

Other Countries

Besides the four tests just outlined, the IISI survey also covered other procedures used in iron and steel plants in the following countries or studied in research centers:

- South Africa and Australia with a procedure fairly similar to the German test method,

- Great Britain with a modified version of the EPA test,
- Italy with two as yet unofficial tests using either water acidified with acetic acid, or water saturated with CO_2. The waste to water ratio is 1 to 16.

Results Obtained in the Iron and Steel Industry Using Different Leaching Tests

Specimens Studied at the IISI

This study was conducted in cooperation with iron and steel laboratories in eight different countries, and we would like to thank them for their kind assistance:

- Australia: Broken Hill Proprietary Co. Ltd.
- England: British Steel Corp-Swinden Laboratories
- France: Leces
- Germany: Thyssen Stahl AG
- Italy: Centro Sperimentale Metallurgico
- Japan: Kawasaki Steel Corporation
- South Africa: ISCOR Limited
- United States: Bethlehem Steel Corporation.

Six different waste materials were leached: two types of slag, one sludge, and three dusts:

(1) LD converter dust (Specimen A),
(2) phosphorous blast furnace sludge (Specimen B),
(3) haematite pig iron desulphurization slag (Specimen C),
(4) electric arc furnace dust (Specimen D),
(5) arc furnace ladle refining slag (Specimen E), and
(6) AOD converter dust (Specimen F).

The six specimens were prepared according to state-of-the-art methods: they were dried, ground to 4 mm, homogenized, and passed through a divider. The chemical characteristics of these specimens are shown in Table 2.

Overall Results

The specimen of LD converter dust was studied alone in 1983. Five different leaching methods were used. Three using deionized (DI) or distilled water, without additives and two based on the EPA method. When leaching with DI water, the pH value attained 11 to 12 in contrast to the pH value of 5 when using the EPA method. The first type determined very low heavy metal concentrations, near or below the detection limit, in all the tests. The EPA methods in contrast determined heavy metal concentrations up to five decimal powers higher. There was a particularly pronounced difference in the concentration of manganese, iron, and zinc. Because of lack of significant results to

TABLE 2—*Chemical characteristics of the different specimens.*

	Specimens[a]					
Composition, %	A	B	C	D	E	F
Fe total	62.9	5.3	29.6	21.0	1.5	35.4
SiO_2	...	4.5	29.1	2.2	10.4	...
CaO	...	2.3	4.9	22.6	53.5	...
Al_2O_3	...	3.2	19.9	0.58	19.7	0.36
TiO_2	...	0.12	1.35	0.11	0.2	0.14
MgO	...	0.33	5.0	1.80	11.4	0.75
P_2O_5	...	0.35	<0.1	<0.1	<0.1	<0.1
MnO	2.86	0.10	7.2	4.45	0.2	11.1
Cd	0.0012	0.012	<0.001	0.014	<0.001	<0.001
Cr	0.154	0.022	0.019	0.538	0.012	13.74
Co	...	<0.001	<0.001	<0.001	<0.001	<0.001
Cu	0.010	0.006	<0.001	0.113	0.061	0.408
Mo	...	<0.001	<0.001	0.033	<0.001	0.846
Ni	0.020	<0.001	<0.001	0.274	<0.001	5.80
Pb	0.255	6.62	<0.001	0.854	<0.001	0.164
Sb	...	<0.001	<0.001	<0.001	<0.001	0.079
V	...	0.013	0.036	<0.001	<0.001	<0.001
Zn	0.34	42.6	0.029	15.5	0.024	0.542

[a]A is LD converter dust. B is BF sludge. C is desulphurization slag. D is arc furnace dust. E is laddle refining slag. F is AOD converter dust.

compare all the leaching procedures, another survey was organized in 1985. Five specimens of wastes, Specimen B to F, were studied according to the leaching procedures described in Table 3. The results obtained are shown in Tables A1 to A5 appendixed to this paper. They differ considerably according to methods and specimens used.

Several parameters seem to predominate: the pH of leachates in equilibrium, duration of mixing, intensity of mixing, number of consecutive leachings, relation between liquid and solid masses, and grain size of waste.

Other parameters can also have an impact on leaching results; these are the presence of CO_2 dissolved in the initial extraction medium and the nature of the acid used in the case of acid extraction procedures. The nature of waste materials, and their physical and chemical characteristics, also have an impact on results.

Impact of Leachate pH

Acidified water ($pH < 4$) is used to simulate how mineral wastes deposited on the surface of the soil interact with rain. This water contains chlorine, sulfate (SO_4), nitrate (NO_3) ions, as well as CO_2 and O_2 in concentrations corresponding to the saturation of rainwater when it comes into contact with the atmosphere. Iron and steel wastes however usually contain high concen-

TABLE 3—*Leaching procedures used for Specimens B to F (IISI survey 1985).*

Laboratories	Waste, g	Rate Water, ml/waste, g	Solvent	Shaking Time, h	Temperature, °C
South Africa	150	10	DI water	1	23
Germany	100	10	DI water	24	room
Australia	350	4	DI water	48	room
France[a]	100	10	DI water saturated with CO_2 and air	24	18 to 25
United Kingdom	400	20	DI water	5	room
Italy 1	100	16	DI water saturated with CO_2	24	15 to 30
Italy 2[b]	100	16	DI water buffered at pH 5 with acetic acid 0.5 *N* Leachate diluted to 2 L	24	15 to 30
Japan	50	10	DI water	6	room
United States[b]	100	16	DI water buffered at pH 5 with acetic acid 0.5 *N* Leachate diluted to 2 L	24	20 to 40

[a]Three successive elutions are required.
[b]EPA method, DI is deionized.

trations of lime, and the pH of leaching water quickly tends to become basic unless acids are added. In point of fact, procedures fall into two categories according to the pH values reached during leaching of the iron and steel products in question:

1. Acid medium extraction procedure, as is the case in particular with the test recommended by the EPA (U.S.-Italy) where the pH must be maintained at 5 through the addition of acetic acid.
2. Extraction procedures inducing an alkaline equilibrium pH (alkalinity imposed by the waste), such as procedures calling for use of raw deionized water or CO_2 saturated water (France-Germany-Japan-Australia- and so forth).

With these two types of procedures, the results obtained in the IISI survey differ considerably for certain elements (Fig. 2). This is particularly true for elements where the precipitation limits of the main hydroxides are not in the same order of size for acid pH and basic pH values. In most cases, the theoretical solubility of heavy metals is lesser with a basic pH than an acid pH, and this is also true for leaching rates of the first type of tests as compared with those of the second type.

The Swinden Laboratories conducted extraction tests on Specimens B, C, D, and F at different pH values, by adding an organic acid (acetic acid) or mineral acid (hydrochloric acid). These various extraction procedures were

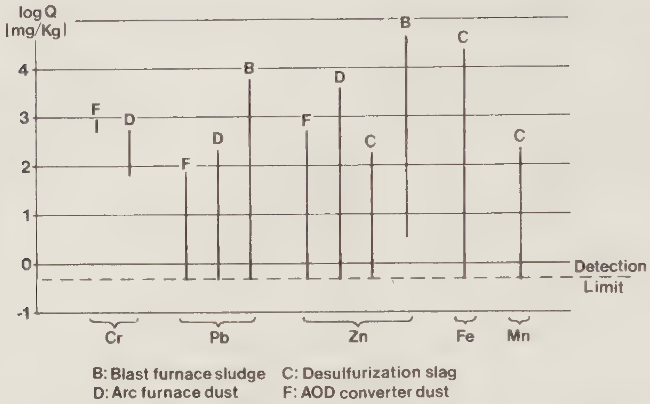

FIG. 2—*Variation of the total quantity of elements extracted* (Q) *during the different leaching-test procedures.*

designed first, to measure the impact of pH variation on the rate of extraction and second, to compare these rates when using an acetic acid (as the EPA test recommends) and a mineral acid.

The results of the study conducted by the Swinden Laboratories are partly shown in Tables 4 and 5. The impact of pH on rates of leaching appears very clearly, with some concentrations varying considerably for relatively slight

TABLE 4—*Impact of equilibrium pH on blast furnace sludge (Specimen B) leaching.*

Solvent Additives, mol/L	pH	Metal Concentration, mg/L					
		Zn	Ni	Mn	Cr	Cd	Pb
			ACETIC ACID				
0	7.5	1.7	<0.5	<0.5	<0.5	<0.5	0.6
0.01	6.6	140	<0.5	0.64	<0.5	<0.5	0.7
0.04	6.3	400	0.05	1.4	<0.05	0.08	5.5
0.1	6.0	2 100	<0.05	2.7	<0.05	0.14	12.8
0.2	5.6	3 400	0.08	4.1	<0.05	0.3	81.6
0.25	5.3	7 300	0.08	5.4	0.08	0.48	380
			HCL				
0	7.5	1.7	<0.05	<0.05	<0.05	<0.05	0.6
0.02	6.3	440	<0.05	1.2	<0.05	0.05	1.2
0.05	6.0	1 200	<0.05	1.9	0.05	0.21	3.6
0.125	5.7	3 000	0.05	3.5	<0.05	0.47	15
0.25	5.3	11 000	0.19	6.8	<0.05	1.57	20
0.3	4.4	8 000	0.11	6.9	0.16	2.4	160
0.375	1.8	11 000	0.26	10.2	4.3	4.2	900

NOTE: Leaching procedure: $L/S = 20$ — deionized water + acid-shaking time 5h.

TABLE 5—*Impact of equilibrium pH on arc furnace dust (Specimen D) leaching.*

Solvent Additives, mol/L	pH	Metal Concentration, mg/L					
		Zn	Ni	Mn	Cr	Cd	Pb
				ACETIC ACID			
0	11.7	3.1	<0.05	0.1	16.0	<0.05	11.2
0.01	11.7	2.3	<0.05	0.1	16.0	<0.05	9.5
0.04	11.4	1.1	0.06	0.1	15.4	<0.05	2.4
0.09	10.6	11.0	<0.05	0.27	13.0	<0.05	1.6
0.10	9.4	0.31	0.1	0.1	12.1	<0.05	<0.05
0.12	8.0	2.7	<0.05	0.18	7.0	<0.05	<0.05
0.17	7.3	100	0.47	0.52	2.58	0.53	<0.05
0.20	5.6	610	1.28	7.8	1.6	2.3	5.8
0.25	5.5	1300	1.73	8.3	1.2	3.4	1.4
			HCL				
0	11.7	3.1	<0.05	0.1	16.0	<0.05	11.2
0.025	11.6	1.9	<0.05	0.07	15.6	<0.05	6.06
0.05	11.0	0.64	<0.05	0.07	17.4	<0.05	0.2
0.10	8.0	6.6	0.1	0.13	0.92	<0.05	<0.05
0.15	6.9	230	1.51	8.1	1.15	1.55	<0.05
0.25	6.2	1000	4.82	47	0.24	4.4	0.7
0.3	6.2	900	6.0	107	0.18	5.4	1.3
0.375	5.8	2700	8.2	100	0.17	6.9	3.7

NOTE: Leaching procedure: $L/S = 20$ — deionized water + acid-shaking time 5 h.

variations in pH. With the blast furnace sludge sample, for example (Table 4), reducing the equilibrium pH from 7.5 to 6 by adding acetic acid, causes a sharp increase in the rate of extraction of certain heavy metals, such as zinc and lead, concentrations of which in the leachate are multiplied by 1235 and 22, respectively. Reducing the equilibrium pH under the same conditions, this time using hydrochloric acid, increases the solubility of zinc 700 times, and the lead extraction rate is at the same time multiplied by a factor of 6.

One thus observes very good correlations between pH and concentration for zinc, manganese, and cadmium in the case of blast furnace sludge and for nickel and cadmium in the case of electric arc furnace dust. Some elements, such as lead and chrome, have a high solubility at both high and low pH values and a lesser solubility at intermediate pH values. An illustration of these relations is shown in Figs. 3*a* and *b* for zinc (Specimen B) and lead (Specimen D).

Specific acid effects can also be observed from the results; for example, more cadmium was leached out by hydrochloric acid than acetic acid from the blast furnace sludge (Specimen B) at comparable pH values, whereas more lead was leached by acetic acid from the same sample at comparable pH values. With many of the other results, specific acid effects may well have been obscured by the scatter of the data.

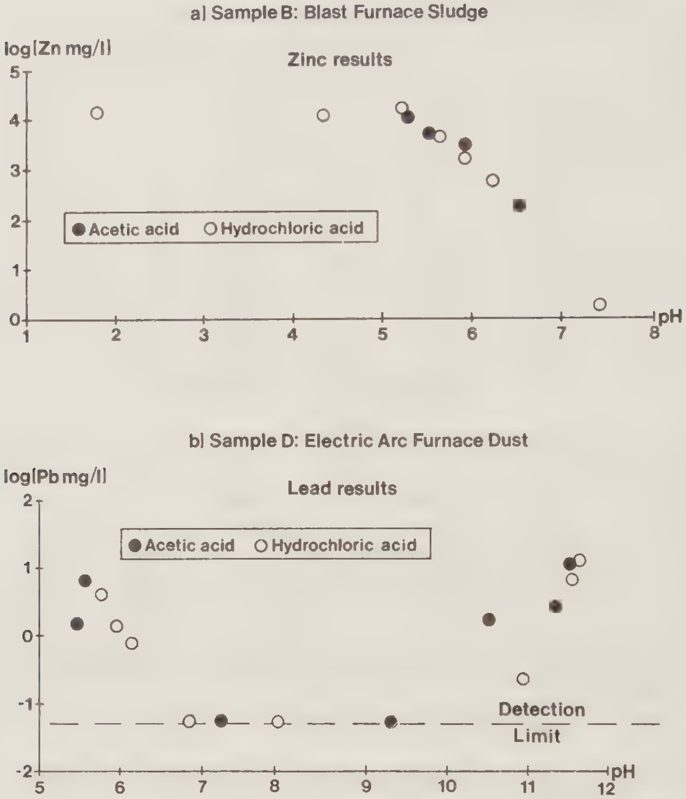

FIG. 3—*Correlation between log (metal) and equilibrium pH* [6]: (a) *zinc results for the blast furnace sludge specimen and* (b) *lead results for the arc furnace dust specimen.*

Impact of Stirring Time

In order for a test to be easily interpreted and repeatable, equilibrium would have to be achieved at the end of leaching of each of the elements solubilized.

This is not possible, for the solubilization of one type of chemical can entail several successive reactions, some of which are irreversible. Inversely, dissolved elements can disappear as a result of parasite reactions, which are not necessarily balanced. The kinetics of a leaching test are therefore very complex. Lee and Plumb [*11*] have defined a typology of the main reactions possible in the kinetic of mineral compound dissolution. Results can therefore vary considerably, subject to the kinetics of leaching and duration of stirring, particularly in the case of a reaction which combines solubilization and adsorption [*12*].

In the circuit set up by the IISI, the water-waste contact times range from 1 h for the South African study to 48 h for the Australian study. By taking a reference specimen, for example, Specimen F (Appendix A3), no significant variation is observed for tests conducted under comparable conditions with the same water/waste ratio: France-Germany-South Africa-Japan. If one takes chromium concentrations as a basis, the impact of stirring time is significant only for durations of less than a few hours. Beyond that, balance is maintained.

Impact of Stirring Conditions

How stirring is done and the intensity with which it is done can have a determinant effect on test results when the conditions of transfer at the solid/liquid interface control dissolution. Over-intensive stirring can also cause abrasion of brittle solid materials and therefore lead to high solubilizations. The ideal stirring process would be one which homogenizes the liquid and renews it at the solid/liquid interface, without altering the physical state of the waste material. In his study, Colin [*8*] showed a preference for stirrers equipped with rollers, such as those used in the Japanese test, the intensity of stirring is determined by the peripheral speed of rotation of the flask wall and seems to be unrelated to the diameter of the flask used.

As regards the leaching procedures used within the framework of the IISI circuit, stirring conditions are often ill-defined. The different techniques used, roller beaters, trippers, blade fans, under normal test conditions induce slow and homogeneous stirring. It can reasonably be assumed, in the absence of further information, that in the various tests used this parameter is a non-discriminating one.

Impact of the Number of Leachings

In order to fully ascertain the toxic dangers of a waste material, it is sometimes advisable to effect several successive leachings by changing the water after each operation. Such is the case with the procedure applied in France. By multiplying the number of leachings for one and the same specimen, one can obtain information about

(1) the evolution in time of leaching waters, particularly their pH,
(2) dissolution kinetics under conditions most akin to reality (succession of rainy and dry periods),
(3) parameters that affect the solubility of pollutants, and
(4) interaction of dissolvable substances.

The first item of information is of particular interest in the case of iron and steel wastes having high lime concentrations, which can gradually decrease as tests progress. In the IISI study, only the procedure applied in France led to

several successive extractions [9]. The results observed show that the kinetics of dissolution generally conform to the same rule, with sharply decreasing concentrations between the first and third extraction, in a ratio of approximately 1 to 10.

An experiment is under way at the INSA in Lyon. Over 20 leachings of 24 h each, according to the French method, have to date been effected on one and the same specimen, with the leaching water being changed every time. Figure 4 shows a clearly antinomic reaction between the dissolutions of calcium (which determines the pH) and hexavalent chromium. The partial results of this study highlight two types of reaction according to the elements considered and the compounds in which they are present. One can observe that

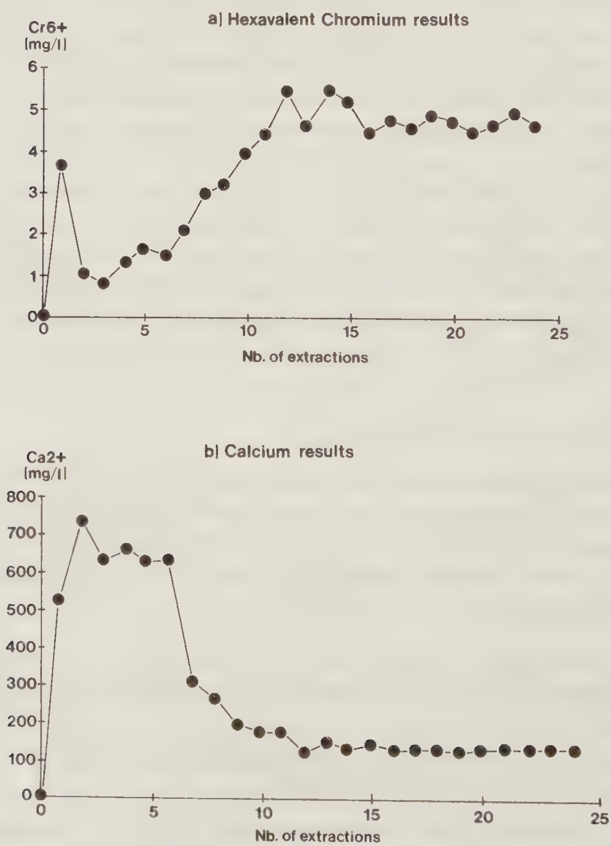

FIG. 4—*Extraction of* (a) *chromium and* (b) *calcium during a repeated leaching test of an electric arc furnace dust.*

(1) leaching is more or less rapid and complete for certain elements such as "free" lime and

(2) leaching is slow and durable as for chromium and a calcium associated phase (calcium oxide [CaO] "combined") always inducing a very high pH.

Impact of Liquid to Solid Mass Ratios

The value of such a liquid to solid mass *L/S* ratio can affect test results in different ways depending on the elements involved:

(1) for very soluble elements, the concentration of leachates is inversely proportionate to the *L/S*,

(2) for less soluble compounds on the other hand, leaching is independent of the *L/S* ratio as long as the liquid is saturated,

(3) in some cases, the *L/S* ratio can effect the concentration of elements likely to be absorbed or desorped from the solid phase, and

(4) the *L/S* ratio can have an indirect effect: elution of the very soluble elements can alter the composition of the leachate and thereby affect the solubilization of low solubility elements.

In the IISI survey, the *L/S* ratio varied between 4 and 20. Its effect is illustrated in the Fig. 5 for the different elements: chromium, zinc, and lead extracted from the arc furnace dust. One can in this case observe two types of reaction, depending on the element concerned: for chromium the quantity dissolved is independent of the *L/S* and for the elements, lead-zinc, the rate of extraction is proportionate to the *L/S* ratio.

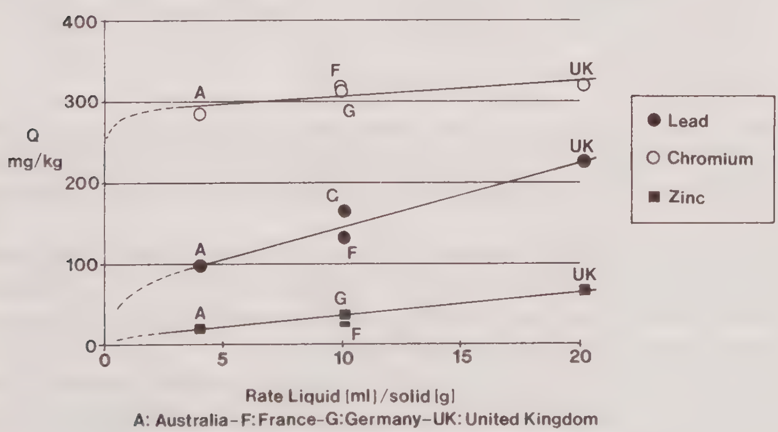

FIG. 5—*Impact of liquid solid ratio on the rate of extraction Q. Comparison with the results obtained on the arc furnace dust specimen.*

Impact of Grain Size of Waste Material

Leaching methods often refer to untreated waste. Most of the time, however, the specimen is crushed or ground, if only to allow for easier handling, particularly when wastes are taken from large volume blocks. Unfortunately, although the object of the test is to find a way of simulating the mechanisms involved, the fact that waste is ground or crushed renders interpretation of leaching test results by extrapolation to the full volume of waste very difficult.

Two extreme cases can be considered:

1. The dissolution of chemical elements is limited to a superficial phenomenon and their speeds must be proportionate to the specific surface of the solid. Ambrose [*13*] for instance shows that arc furnace dust pellets bound without cement but uncrushed can, even if they exfoliate, lead to lower leaching rates, about five times for cadmium and zinc, than with the same but pre-crushed products.
2. The entire waste mass is involved in leaching and the speed of dissolution becomes independent of grain size.

In the IISI survey, all leached specimens were subject to the same cycle of mechanical preparation. Slag specimens (Specimens C and E) were therefore pre-crushed to obtain a sieve fraction of less than 4 mm. Crushing or grinding, however, produces unnatural fines, which if taken into account, can falsify the results obtained [*6*]. Within the scope of the IISI survey so as to obtain homogeneous specimens, the fine fraction of less than 0.5 mm was removed before leaching.

Moreover, so as not to mistake the elements really dissolved and those eluted with the ultra-fine particles, all the leaching procedures outlined in the IISI survey call for leachate filtering at 0.45 μm, with the threshold by definition distinguishing the dissolved fraction from the particle fraction.

Impact of the Nature of the Waste Material

The IISI survey results illustrate how leaching results can vary for waste materials from different plants using one and the same procedure. The same is true for one and the same type of plant according to metallurgical conditions.

This is highlighted by comparative studies published in the United States [*14,15*]. For instance, the leaching-test results conducted on 47 specimens of arc furnace dusts show levels ranging between 0.01 and 8.3 mg/L for cadmium and between 0.01 and 376 mg/L for lead.

Such results are due to the nature of the waste in question, not only to their chemical composition, but also to their mineralogical composition. Zinc combined with stable ferrites, for example, is virtually unleached.

The very complex case of chromium must also be mentioned [*16–18*]. This

element more frequently features Valences 3 and 6, the soluble salts of which have different toxicities. By confining oneself to dusts that have been subject to high temperatures, several phases can be envisaged: sesquioxides chromic oxide (Cr_2O_3) and III and VI chromium salts soluble or insoluble in water. A study made in France [*16*] in the leaching of arc furnace dust revealed a fairly high dispersion of chrome dissolution results.

This leads to the assumption that dust reacts very differently depending on the nature of metallurgical operations and processes and the intensity of reactions occurring in the fumes between chrome oxide Cr_2O_3 and lime, both in powder form in the presence of oxygen.

Comparison of Leaching Results and Toxicity Thresholds

The leaching test provides for a simple modelling of water/waste interactions according to specific experimental standards that do however often differ from one country to the next. On the basis of the established methodology of the leaching test, concentration thresholds have been defined, as discussed in Chapter 2, with a view to controlling the disposal of potentially toxic wastes.

If we consider the six specimens, A to F, tested according to the national standards or draft standards published in the United States, France, and Japan, it is possible to point out the toxic wastes that present for one element at least a rate, experimental value (EV)/concentration threshold (CT), greater than 1. On the basis of the results presented in Table 6, it was observed that

1. The test recommended by the EPA has discreting results in the case of products rich in heavy metals and containing few alkaline elements; the blast furnace sludge sample (Specimen B) is a typical example. According to regulations in force in the United States, the lead extracted using the EPA method, is 54 times in excess of the standard, whereas it is more than 100 times below the standard imposed for the French and Japanese tests.

TABLE 6—*Classification of wastes by leaching tests. Comparison between experimental values (EV) and concentration thresholds (CT) defined by national standards or draft standards in the United States, France, and Japan.*

	Elements with EV/CT > 1					
	United States		France		Japan	
Hazardous Wastes	Elements	EV/CT	Elements	EV/CT	Elements	EV/CT
Blast furnace sludge	Pb	54	...	...	...	...
Arc furnace dust	Cr total	3.4	Cr VI	>4	Cr VI	18.8
AOD converter dust	Cr total	9	Cr VI	>4	Cr VI	42

NOTE: The concentration thresholds CT are shown in Table 1.

2. For the total volume of waste, excluding the case outlined above, the only critical element observed, which oversteps authorized thresholds, is chromium, present in these samples essentially in the form of Cr VI. The two offending wastes materials are arc furnace dust (Specimen D) corresponding to the production of special steels and argon-oxygen-decarbonization (AOD) converter dust used to manufacture stainless steel.

The strictest standards are those laid down by the Japanese regulation with the authorized threshold being exceeded 20 and 40 times, as opposed to only 3.5 to 9 times in the case of the regulation based on the EPA test. As the French draft regulation concerning Cr VI is based on the concentrations measured on the total volume of waste, it is not known by exactly how much the threshold is exceeded. In any case, since chromium is present in waste mainly in the form of Cr VI, according to test results, the recommended threshold of 100 mg/kg is very largely exceeded; in borderline cases, the problem of Cr VI dosage in solid state does nevertheless arise, as conventional wet process methods are still not very reliable in this respect.

Conclusion

We have just presented a number of results taken from an international comparison conducted at the instigation of the IISI Environment Committee and which have been supplemented with information extracted from several other studies conducted in Germany, France, Great Britain, and the United States. The different methods implemented are designed to simulate water/waste interaction phenomena by reproducing natural disposal and depositing conditions as closely as possible. Consequently,

1. The EPA procedure for acid medium extraction by the addition of acetic acid sets out to simulate the effect of organic acids on mixed waste materials including household waste and industrial waste and
2. The use of demineralized CO_2 saturated water is intended to simulate the aggressivity of meteoric waters.

When it comes to defining a model of the dangers involved, an ideal leaching test is impossible to achieve. If the test can be made as realistic as possible by adapting certain parameters, pH-water/waste ratio, there will always remain an unknown factor, namely, the site factor which renders all ecotoxic interpretations hypothetical. A leaching test cannot in itself provide insight into the complexity of ion exchanges between waste, water, and natural environment (clays, organic matter, and so forth).

The leaching test does nevertheless offer the advantage of providing for good characterization of waste materials in terms of solubility. It is possible, with a test of this kind, to evaluate both quantitatively and qualitatively the soluble fraction of a waste material. It is therefore quite conceivable, within

the scope of the International Standards Organization (ISO) for example, to develop a simple and specific leaching process that could be universally adopted as a unique characterization test. One could also conceive completing it by introducing ecotoxicological considerations.

Whatever the nature of laboratory studies, whether they concern leaching or take into account ecotoxicological factors, one must not lose sight of the fact their final objective is to allow for an assessment of the real risks involved in waste disposal to be made. Results must therefore be such that they can be interpreted according to mathematical models. Such models are beginning to emerge [*19,20*], but further improvements will no doubt have to be made.

APPENDIX

The following tables provide leaching-test results for Specimens B to F using different procedures. Descriptions are given in Table 3.

TABLE A1—*Leachate characteristics of Specimen B, BF sludge.*

Analysis Items	France	United States	Germany	Australia	South Africa	Japan	United Kingdom	Italy 2	Italy 1
pH	7.6	5	8.37	7.65	7.30	8.0	7.5	5	?
As, mg/L	. . .	<0.5	<0.01	0.01	<0.01	<0.01	. . .	<0.01	<0.01
Cd, mg/L	<0.05	0.33	<0.01	0.01	<0.01	<0.01	<0.05	0.04	0.01
Cr total	<0.05	<0.1	<0.04	<0.01	<0.05	<0.05	<0.05	<0.05	0.07
Ni, mg/L	<0.05	<0.1	<0.04	<0.01	<0.01	<0.01	<0.05	0.10	<0.05
Pb, mg/L	<0.05	290.0	0.09	0.04	<0.01	0.05	0.57	<0.01	<0.01
Zn, mg/L	6.8	2600	0.61	0.89	0.86	0.39	1.7	2580	17.0

TABLE A2—*Leachate characteristics of Specimen C, desulfurization slag.*

Analysis Items	France	United States	Germany	Australia	South Africa	Japan	United Kingdom	Italy 2	Italy 1
pH	6.45	5	10.86	11.02	10.2	10.0	9.3	5	. . .
As, mg/L	. . .	<0.05	<0.01	<0.01	<0.01	<0.01	. . .	0.01	<0.01
Cd, mg/L	<0.05	<0.05	<0.01	<0.01	<0.01	<0.01	<0.05	<0.05	<0.05
Cr total	<0.05	<0.1	<0.04	0.01	<0.05	0.01	<0.05	<0.05	<0.05
Fe, mg/L	90.0	. . .	0.04	0.09	0.09	1.64	. . .	1036	26.0
Mn, mg/L	7.4	. . .	<0.02	0.01	<0.05	0.07	0.07	16.0	3.2
Zn, mg/L	<0.05	0.7	0.02	<0.01	<0.01	0.02	0.20	9.0	<0.01

TABLE A3—*Leachate characteristics of Specimen D, arc furnace dust.*

Analysis Items	France	United States	Germany	Australia	South Africa	Japan	United Kingdom	Italy 2	Italy 1
pH	12.50	5	12.59	12.52	...	12.8	11.7	5	...
As, mg/L	...	<0.05	<0.01	0.02	...	<0.01	...	0.20	0.14
Cd, mg/L	<0.05	0.05	<0.01	0.02	...	<0.01	<0.05	0.04	<0.01
Cr total	31.4	17.0	31.0	71.0	...	29.9	16.0	4.0	23.0
Ni, mg/L	<0.05	<0.1	<0.04	<0.01	...	<0.01	<0.05	0.33	<0.05
Pb, mg/L	13.3	<0.1	16.0	23.6	...	1.5	11.2	<0.01	<0.01
Zn, mg/L	3.05	<01	3.5	4.3	...	0.03	3.1	184.0	<0.02

TABLE A4—*Leachate characteristics of Specimen E, laddle refining slag.*

Analysis Items	France	United States	Germany	Australia	South Africa	Japan	United Kingdom	Italy 2	Italy 1
pH	11.9	5	12.57	12.18	11.50	12.5	11.0	5	...
As, mg/L	...	<0.05	<0.01	0.01	<0.01	<0.01	...	0.06	0.04
Cd, mg/L	<0.05	<0.05	<0.01	<0.01	<0.1	<0.01	<0.05	0.08	<0.05
Cr total	<0.05	<0.1	<0.04	<0.01	<0.5	0.04	<0.05	0.08	<0.05
Ni, mg/L	<0.05	<0.1	<0.04	<0.01	<0.1	<0.01	<0.05	<0.01	<0.01
Pb, mg/L	<0.05	0.1	0.38	<0.01	<1.0	0.01	<0.05	<0.01	<0.01
Zn, mg/L	<0.05	<0.1	0.13	<0.01	<0.1	0.05	<0.05	<0.02	<0.02

TABLE A5—*Leachate characteristics of Specimen F, AOD converter dust.*

Analysis Items	France	United States	Germany	Australia	South Africa	Japan	United Kingdom	Italy 2	Italy 1
pH	11.87	5	11.75	12.25	11.80	11.5	...	5	...
As, mg/L	...	0.06	<0.01	0.06	<0.01	<0.01	...	0.09	0.02
Cd, mg/L	0.05	0.22	<0.01	0.03	<0.01	<0.01	...	0.02	<0.01
Cr total	68.0	45.0	69.0	170.0	84.8	54.2	...	30.0	36.0
Ni, mg/L	<0.05	5.2	<0.04	<0.01	0.07	0.01	...	0.33	0.11
Pb, mg/L	<0.05	0.1	0.45	5.4	<0.1	0.04	...	<0.01	<0.01
Zn, mg/L	<0.05	24.0	<0.02	<0.01	<0.01	0.04	...	3.0	<0.02

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Comparison of Leachate Quality in Foundry Waste Landfills to Leach Test Abstracts

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ABSTRACT: The landfills for six ferrous foundries in Wisconsin were instrumented with suction lysimeters to sample leachate directly from the waste above the zone of saturation. All landfills disposed of only foundry process solid wastes had minimal known changes in processes and waste over the period of landfilling in the areas tested and were not located in ground water. The quality of leachate from the lysimeters was compared to the quality of leachate obtained by laboratory leach testing of the auger cuttings obtained during lysimeter installation and to leach tests performed on composite raw waste samples obtained directly from the foundries.

It is concluded that, even though the (EP) (acid) test was able to predict the presence or absence of a contaminant in landfill leachates over half of the time, the test was inaccurate, in some cases grossly inaccurate, in predicting the actual field concentrations. It is also concluded that the EP (water) test was basically equal to the EP (acid) test in being able to predict the presence of absence of a contaminant in landfill leachates.

KEY WORDS: foundry wastes, landfills, leach tests, ground-water quality, leachate quality

The objective of the work presented here was to compare results from laboratory leach tests on foundry process solid wastes to leachate quality within the corresponding landfills. This was part of a larger project to investigate the leaching characteristics of foundry wastes and water quality within and adjacent to landfills containing only foundry process solid wastes [*1*]. The portion of the work described here was carried out by the University of Wisconsin;

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however, it should be noted that Residuals Management Technology, Inc. (RMT), a consulting engineering firm located in Madison, WI, worked on the overall project as a coinvestigator. RMT compiled data developed previously for various clients of their business that were pertinent to this study.

It is important to examine the relationship between the extraction procedure (EP) test (using acetic acid) and actual landfill leachate quality because in the United States the leaching test is used to classify wastes as hazardous or not for regulatory purposes under a federal law called the Resource Conservation and Recovery Act (RCRA). There are no published data known to the authors that examine the validity of the leach test and its relationship to field results. This is critical in that the test is being used to make major decisions involving huge amounts of money and resources, and potentially putting some companies out of business. The method involved the University working with six ferrous foundries in the Wisconsin area to look particularly at leachate quality within the landfilled waste and to compare these results with leachate quality arising from laboratory extractions of the waste.

To do the work described in this paper, it was necessary to avoid dilution or attenuation effects or both on leachate quality as a result of sampling in the saturated zone in or under the foundry waste landfills. Such effects would have been difficult to quantify at best and would have required much more data and interpretation to meet the objectives of the study. Accordingly, it was necessary to sample in the unsaturated zone within the waste. This means that comparisons between field leachate quality as presented here and leach test results should be as good as could be expected since factors extraneous to the leaching process itself were minimized.

Method

One of the difficulties of sampling the unsaturated zone is the necessity to use pressure-vacuum lysimeters. Further, to minimize leachate-lysimeter interactions, it was decided to use Teflon® lysimeters as shown in Fig. 1. In concept, the idea is to place this device in the 17.5-cm-diameter hole drilled into the landfill above the water table, backfill the hole, and then place a vacuum sufficient to overcome capillary forces holding moisture in the waste. Moisture is thereby pulled into the lysimeter for sampling. By this means, leachates that have been in intimate contact with the waste are sampled without having to worry about dilution by ground water or any attenuation effects. This device is much more difficult to install and operate than a well point, but with experience samples of adequate size for analysis were obtained in most cases. Each lysimeter produced at least two samples, unless noted otherwise; most lysimeters produced from four to six samples.

Figure 2 is a rough map showing the Foundry A landfill as an example of one of the six university test sites. This particular foundry is a gray and ductile iron foundry with a total melt in 1981 of approximately 8100 metric tons per

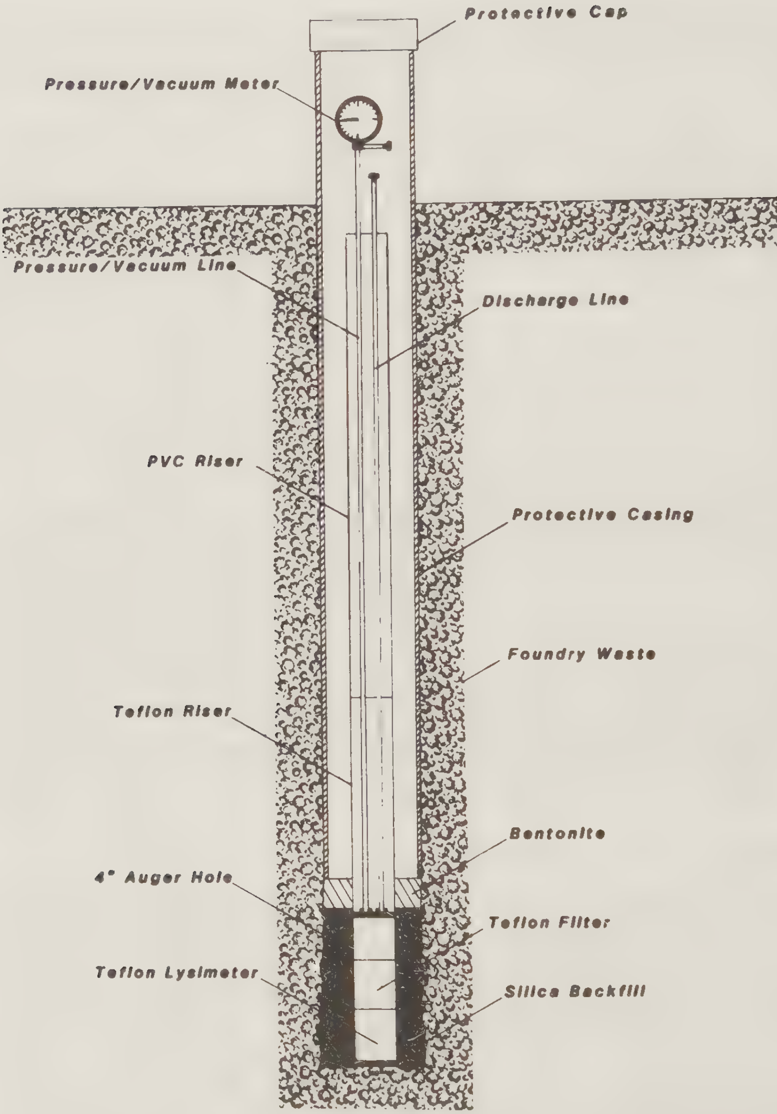

FIG. 1—*Typical pressure vacuum lysimeter installation.*

year. The landfill was nine years old and was continuing in operation at the time of this investigation. It is 30 km^2 (3 hectares) in area and the depth of the waste is approximately 3 m. It contained only foundry process wastes, as did all foundry landfills tested in this study.

Table 1 presents the typical percentage of materials to a foundry waste landfill. The different foundry processes producing wastes within a foundry

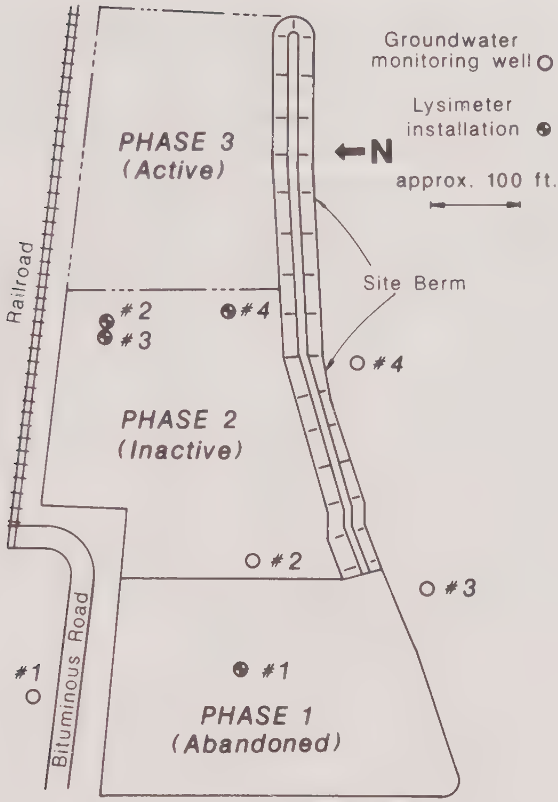

FIG. 2—*Foundry "A" landfill.*

TABLE 1—*Typical percentage of materials to foundry waste landfills from iron foundries* [2].

Material	Typical Percentage[a] of all Waste to Landfill
Refractory	1.09 to 2.25
Total Sand	65.61 to 87.71
system sands	51.83 to 70.12
core sands	3.58 to 17.60
Annealing room waste	0.0 to 2.47
Cleaning room waste	0.52 to 3.02
Slag and ash	5.39 to 16.34
Scrubber and dust collector discharge	1.12 to 11.96
Miscellaneous	0.0 to 0.29

[a]All values based on results of three iron foundries.

produce wastes of widely different characteristics, which will be of interest if one attempts to change the leaching characteristics of all the wastes produced from a given foundry. The various wastes are taken to the landfill as the containers receiving them are filled and dumped on the working face. Individual wastes are therefore to be found throughout the landfill but may exist in "pockets" where a particular container or truck was dumped.

One of the problems encountered results from this variability in waste composition in a foundry waste landfill. One might think that foundry wastes and the corresponding leachates would be of uniform composition and so could be easily sampled and tested. In fact, both are quite variable. Not only was leachate quality found to be variable from point to point within any landfill, but it was variable at a given lysimeter from one sample to the next. For example, the iron concentrations at Lysimeter 1 for Landfill A varied over the 14-month period of monitoring from less than the detection limit of 0.004 to 0.912 mg/L. There was no trend in concentration with time; in fact, the lowest and highest values were measured 1½ months apart at the end of the monitoring period. It is difficult to define the iron content of the leachate from such data. An additional problem is the fact that many species analyzed were at concentrations below the analytical detection limits because all eight metals for which there are primary drinking water standards were to be analyzed whether or not they were likely to be present.

In order to reduce data showing great variability and where values are frequently below detection limits, a log-normal probability distribution was utilized as shown in Fig. 3 using iron from Foundry A as an example. The coordinate labeled percentage indicates the percentage of the samples analyzed that were at or below the corresponding concentration of iron shown on the vertical scale. From Fig. 3, for example, 50% of the samples had approximately 0.1 mg/L of iron or less. Similarly, 95% of the samples had a concentration less than 3 mg/L of iron, and so forth. The goodness of fit shown in Fig. 3 is typical of that for other chemical species, lysimeters, and foundry landfills.

Laboratory leach tests were performed on wastes removed by the auger in the process of installing lysimeters or on wastes composited from the various waste sources in the foundry in proportion to their generation rates. The leaching test procedure used is the so-called EP test [*3*], which is required by the U.S. Environmental Protection Agency (EPA) to classify a waste as hazardous or not with respect to leaching characteristics. The procedure basically involves subjecting the waste in question to pH 5 acetic acid in a slowly rotating or tumbling container. The waste to liquid ratio is 1 to 20 by weight. The pH of the mixture is checked after specified time intervals of mixing and the pH adjusted to 5 ± 0.2 if necessary by the addition of more acid or base. After approximately 24 h of mixing, the extract is separated from the waste by 0.45-μm filtration and analyzed. This test will be referred to as the EP (acid) test in this paper.

Even though the selection of pH 5 acetic acid as the leaching medium was

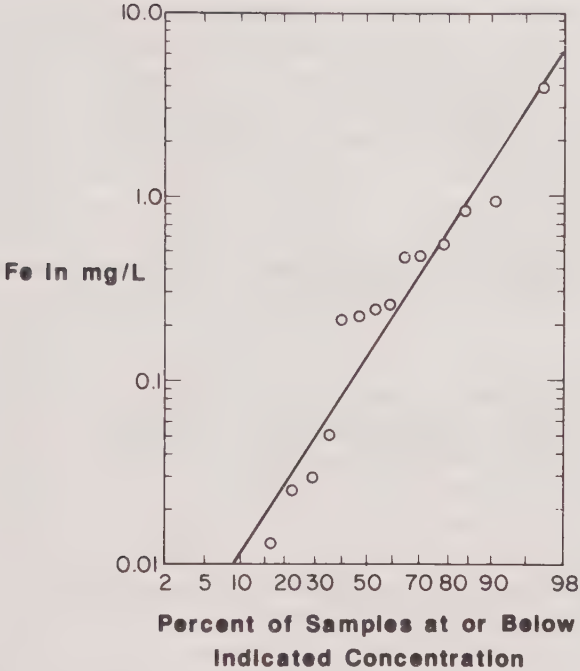

FIG. 3—*Iron at foundry landfill "A"*.

based on municipal refuse sanitary landfill leachate characteristics, the EP (acid) test is used to classify a waste whether it is to be disposed by itself (a monofill) or with other wastes such as municipal refuse. Considering that many foundry process wastes are disposed in monolandfills, including all landfills studied here, it was thought that field conditions would be more closely approximated in the laboratory by using deionized water as the leaching medium. The procedure referred to here as the EP (water) test is the same as the EP (acid) test except deionized water is substituted for the pH 5 acetic acid, and pH adjustments are not made during mixing.

Analyses for metals were performed with a Perkin-Elmer atomic absorption spectrophotometer, for fluoride with an Orion specific ion electrode, for total organic carbon (TOC) with a Beckman Model 915 analyzer, and the colorimetric procedure for phenols used a Beckman DU-2 spectrophotometer. All analyses were performed and samples prepared according to standard procedures as given in Ref *4*.

Results

Table 2 presents the summarized data for Foundry F as an example of the results. Table 2 indicates that the drinking water limit for arsenic is 0.05 mg/

TABLE 2—*Foundry F: composite leaching test results and field leachate results.*

Component	U.S. EPA Drinking Water Standard/ Criteria	Detection Limit	EP (Water) Composite Waste Batch Leaching Test	EP (Acid) Composite Waste Batch Leaching Test	Field Leachate 20%	Field Leachate 50%	Field Leachate 95%[a]
Arsenic	0.050	0.005	BDL	BDL	BDL	BDL	BDL
Barium	1.000	0.46	BDL	BDL	BDL	BDL	BDL
Boron	1.000	0.7	BDL	BDL	BDL	BDL	BDL
Cadmium	0.010	0.001	BDL	BDL	BDL	BDL	0.018
Chromium	0.050	0.003	BDL	BDL	BDL	BDL	0.130
Copper	1.000	0.002	BDL	BDL	BDL	BDL	0.100
Iron	0.300	0.004	BDL	66.25	0.14	0.71	16.2
Lead	0.050	0.01	BDL	BDL	BDL	BDL	BDL
Manganese	0.050	0.002	BDL	2.88	0.054	0.13	0.70
Mercury	0.002	. . .	. . .	. . .	0.0021[b]	0.0032[b]	0.0075[b]
Selenium	0.010	0.13	BDL	BDL	BDL	BDL	BDL
Silver	0.050	0.002	BDL	BDL	BDL	BDL	BDL
Zinc	5.000	0.001	BDL	0.402	0.026	0.068	0.420
TOC	. . .	. . .	12.0	. . .	. . .	30	. . .
Phenols	0.300	0.05	. . .	. . .	BDL	BDL	BDL
Cyanide	0.200	0.02	. . .	. . .	BDL	0.10	0.24
Fluoride	1.400	0.4	2.1	1.0	2.9	4.1	8.3
pH	. . .	. . .	8.7	. . .	. . .	7.8	. . .
Specific Condition	. . .	. . .	. . .	. . .	. . .	3.5×10^3	. . .

NOTE: All units are mg/L except for specific conductivity, which is in μS/cm, pH BDL = below detection limit.

[a]Percent of all samples analyzed at or below the concentration shown.

[b]Indicates one of seven samples above detection limits, thereby increasing the estimated concentration at any given probability. See text for a discussion of detection limits.

L while the detection limit experienced here was 0.005. All laboratory and field leachates associated with Foundry F had arsenic values less than the detection limit as shown in the five columns. Column 3 gives the results using the EP (water) test on composite wastes mixed to represent the overall waste produced by the foundry. Column 3 indicates that the leachate resulting from mixing deionized water and composite Foundry F waste was below the detection limit for arsenic, which was in turn 10% of the drinking water standard for arsenic. The fourth column presents the results using the EP (acid) test with the eluant adjusted to pH 5 with acetic acid, according to the EPAs procedure. Once again, the resulting leachate was below the analytical detection limit for arsenic for Foundry F.

The last three columns present the results from the lysimeter samples of leachate in contact with the waste in the landfill. These results are presented at the 20, 50, and 95% levels for all samples analyzed from Foundry F. All three columns indicate values less than the analytical detection limit for arsenic. At the 95% level, for example, the results indicate that 95% of all the samples analyzed were less than the analytical detection limit for arsenic.

Iron is a little more interesting in that some values shown in Table 2 are above the analytical detection limit of 0.004 mg/L. The drinking water standard for iron is 0.3 mg/L. Iron is not a primary contaminant, but it is a secondary contaminant. This means that iron does not have known health implications, but it might cause problems from aesthetic, taste, or odor properties. The EP (water) test on the waste composite gave an iron concentration below the detection limit. The EP (acid) test, which is run at pH 5 $\pm$ 0.2, resulted in iron leached from the waste, reaching a concentration of 66 mg/L. The EP (acid) procedure is interpreted by a criterion that states that a waste is EP toxic and would be declared a hazardous waste if a primary drinking water contaminant were leached from the waste and attained a concentration in the leachate equal to or greater than 100 times the drinking water standard for that contaminant. Since iron is only a secondary contaminant, this criterion has no application here, but it is used here to illustrate that this waste would be considered to be a problem with respect to iron leaching characteristics if iron were a primary contaminant. The 50% field leachate iron concentration was 0.71 mg/L, which was about twice the drinking water standard. Ninety-five percent of all samples were less than 16.2 mg/L. Looking at the remaining 50% field leachate results, it is observed that values were at or below the drinking water standard for all primary metals and that only in the case of iron, manganese, and fluoride were values obtained above drinking water standards.

The results from mercury are somewhat incomplete as indicated in Table 2. A relatively large sample size is required to analyze for mercury. Given this fact plus the low levels of mercury typically found in foundry landfill leachates and the inability to always obtain sufficient sample to run all analyses, mercury was not run as frequently as the other elements. Further, in order to run

mercury at all, deionized water known to contain no mercury was frequently added to the field samples to have enough sample for analysis. This means that the detection limit changed from sample to sample, and only in the case of no dilution would the detection limit approach the drinking water standard of 0.002 mg/L.

Table 3 presents a summary of all six foundry field leachate composition results using the 50% or median values. The 50% results are emphasized because these are the values most likely to be observed and so represent the impact of the waste on leachate quality. There is a chance a lower value would be obtained (for example, the 20% value) or a higher value (for example, the 95% value), but such values are a result of the nonhomogeneous nature of a foundry waste landfill and are not indications of the realistic impact of the landfill on the environment. Notice in Table 3 that with respect to most of the water quality parameters evaluated, the level shown is well below the drinking water standard. Arsenic is again a good example of this group of parameters. Primary drinking water standards exist for arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. With the exception of Foundry B for lead and Foundry E for chromium, none of the leachate samples taken directly from the waste in the landfills were above primary drinking water standards used in classifying a waste as hazardous or not. The values of the two exceptions were 1.2 and 2 times the standard, respectively, which is well under the hundred-fold criterion used in the EP toxic classification. Considering that such leachates may be expected to be the most concentrated leachates, in that they were in direct contact with the waste and had no groundwater dilution, these landfills do not appear to be a threat to ground-water quality with respect to primary parameters. With respect to secondary parameters, there are three values for iron above the drinking water standard, and every foundry was greater than the drinking water standard for manganese. Both iron and manganese standards relate to aesthetics, as both elements present a staining characteristic and in some cases relate to taste. Fluoride is a primary contaminant, but is not used in classifying a waste as EP toxic. Three of the landfills had median levels above the 1.4-mg/L standard (depending on temperature, the alternate standard is 2.4 mg/L).

Table 4 gives the comparison between the EP (water) test results when run on a waste composited to be representative of the waste generated by the foundry and leachate quality in the corresponding landfilled waste. For each parameter, there is either a 1 or 0 at the 50 or 95% of all samples analyzed level for each of the six foundries. The 50% level is probably the more interesting in that it represents a "typical" level. A number 1 indicates that the leach test in the laboratory predicted the presence or absence of a parameter in the field leachate. A number 0 indicates that the prediction was not correct. In this case, a parameter may have been present in the field and not picked up in the laboratory or it might have not been present in the field and

TABLE 3—*Median field leachate results of all foundries A through F.*

Leachate	Foundry A[a]	Foundry B	Foundry C	Foundry D	Foundry E	Foundry F
Arsenic	BDL	BDL	BDL	BDL	BDL	BDL
Barium	BDL	BDL	BDL	BDL	BDL	BDL
Boron	BDL	BDL	BDL	BDL	BDL	BDL
Cadmium	BDL	BDL	BDL	BDL	BDL	BDL
Chromium	BDL	BDL	BDL	BDL	0.10	BDL
Copper	0.007	BDL	0.021	0.014	0.084	BDL
Iron	0.14	1.40	0.30	0.18	0.49	0.71
Lead	BDL	0.06	BDL	BDL	BDL	BDL
Manganese	1.10	0.16	0.056	0.052	0.10	0.13
Mercury	<0.0033	<0.0085	<0.0040	<0.0059	<0.0075	<0.0029
Selenium	BDL	BDL	BDL	BDL	BDL	BDL
Silver	. . .	BDL	BDL	BDL	BDL	BDL
Zinc	0.14	0.28	0.059	0.056	0.27	0.068
TOC	105	21	13	41	26	30
Phenols	BDL	BDL	BDL	BDL	BDL	BDL
Cyanide	0.06	BDL	BDL	0.06	. . .	0.10
Fluoride	BDL	BDL	0.5	9.6	2.0	4.1
pH	8.2	7.1	7.4	8.0	8.0	7.8
Specific Conductivity	1.0×10^3	1.2×10^3	1.5×10^3	2.5×10^3	. . .	3.5×10^3

NOTE: BDL: below detection limit (values given in Table 2). Drinking water standards/criteria and units given in Table 2.
[a]Results of Foundry A do not include Lysimeter 2.

TABLE 4—*Comparison of composite EP (water) leaching test and unsaturated zone field leachate.*

	Foundry A[a]		Foundry B		Foundry C		Foundry D		Foundry E		Foundry F	
Leachate	50%	95%	50%	95%	50%	95%	50%	95%	50%	95%	50%	95%
Arsenic	1	1	1	1	1	1	1	1	1	1	1	1
Barium	1	1	1	1	1	1	1	1	1	1	1	1
Boron	1	1	1	1	1	1	1	1	1	1	1	1
Cadmium	1	0	1	1	1	0	1	0	1	0	1	0
Chromium	0	1	0	0	1	1	1	0	0	0	1	0
Copper	1	1	1	0	0	0	0	0	0	0	1	0
Iron	1	1	0	0	1	1	0	0	1	1	0	0
Lead	1	0	0	0	1	1	1	0	1	1	1	1
Manganese	1	1	0	0	1	1	0	0	1	1	0	0
Mercury	...	...	...	...	...	...	...	...	...	...	...	...
Selenium	1	1	1	1	1	1	1	1	1	1	1	1
Silver	1	0	1	1	1	1	0	0	1	1	1	1
Zinc	1	1	1	1	1	1	0	0	0	0	0	0
Phenols	0	1	...	...	...	...	...	...	...	...	...	...
Fluoride	0	1	0	1	0	0	1	1	1	1	1	1

NOTE: Number of successful predictions at 50% (as predicted by a 1) = 58 out of 79. Percent successful predictions = 73%. Number of successful predictions at 95% (as predicted by a 1) = 50 out of 79. Percent successful predictions = 63%.

[a]Results for Foundry A do not include Lysimeter 2. 50% = median concentration of field leachate samples. 95% = concentration below which 95% of all field leachate samples fall. 0 implies that this parameter not predicted by the batch leaching test but present in field leachate or parameter predicted by batch leaching test but not present in field leachate. 1 implies that this parameter not predicted by batch leaching test and not found in field leachate or this parameter predicted by batch leaching test and found in field leachate.

found in the laboratory. It turns out that at the 50% level, 58 out of 79 predictions were successful for a success rate of 73%.

Table 5 gives results comparable to Table 4 except the EP (acid) test results on composite wastes using pH 5 acetic acid are compared to field leachate quality. The number of successful predictions of 50% of all field samples analyzed results is 60 out of 78 total for a success rate of 77%. This is basically the same as obtained with the EP (water) test.

Continuing to compare only at the 50% field level, Table 6 indicates that for the EP (acid) test on auger cuttings, there were 68 successful predictions out of a total of 81 for a success rate of 84%. The corresponding table with the results of the EP (water) test on auger cuttings is not given here, but 68 successful predictions were obtained out of 82 for a success rate of 83%. Once again, the EP (acid) and EP (water) tests were virtually identical in their ability to predict the presence or absence of a specific parameter in the 50% of all samples analyzed as unsaturated zone field leachate samples. Comparing the percentage of successful predictions for the composite versus the auger cuttings, both the EP (acid) and EP (water) tests gave a slightly better success rate when auger cuttings were used. This is reasonable since the field leachate samples came from the immediate vicinity of the auger cuttings, and there was no assurance that the wastes in this area were representative of the overall wastes as generated.

The EP (acid) and EP (water) tests achieved approximately the same success rate in that the overall percentages of successful predictions were essentially the same. It is useful to note, however, the EP (water) procedure had no erroneous predictions for cadmium, while the EP (acid) procedure was incorrect a total of six out of twelve times for the composite and auger samples. The EP (water) procedure was also better in predicting lead (three unsuccessful predictions for EP [water] versus six for the EP [acid] out of twelve evaluations). On the other hand, the EP (acid) procedure better predicted manganese and zinc for the composites in particular, and copper for the auger samples. All of these comments are based on the 50% of all samples analyzed as field levels. The results at the 95% level are similar but with a slightly lower successful prediction rate.

Table 7 is a summary of the comparisons between the 50% field leachate concentrations and the composite waste EP (acid) concentrations. In this case, the ratios of the field to the EP (acid) concentrations are given, so a value of 1.0 indicates a perfect prediction, not only of the presence or absence of a parameter in the field but also its concentration. A value less than 1.0 indicates that the EP (acid) test overestimated field concentrations while a value greater than 1.0 indicates that the EP (acid) test underestimated field concentrations. In almost every case, a value of 1.0 is seen to indicate the EP (acid) test successfully predicting the absence of a parameter in the field.

One could argue that a successful test would at least not produce values consistently above or below field concentrations. This recognizes that it would

TABLE 5—*Comparison of composite EP (acid) leaching test and unsaturated zone field leachate.*

	Foundry A[a]		Foundry B		Foundry C		Foundry D		Foundry E		Foundry F	
Leachate	50%	95%	50%	95%	50%	95%	50%	95%	50%	95%	50%	95%
Arsenic	1	1	1	1	1	1	1	1	1	1	1	1
Barium	1	1	1	1	1	1	1	1	1	1	1	1
Boron	1	1	1	1	1	1	1	1	1	1	1	1
Cadmium	1	0	0	0	0	1	1	0	0	1	1	0
Chromium	0	1	0	0	0	0	1	0	0	0	1	0
Copper	1	1	1	0	0	0	0	0	0	0	1	0
Iron	1	1	0	0	1	1	1	1	0	0	1	1
Lead	1	0	0	0	0	0	1	0	0	0	1	1
Manganese	1	1	1	1	1	1	1	1	1	1	1	1
Mercury	...	...	...	...	...	...	...	...	...	...	...	...
Selenium	1	1	1	1	1	1	1	1	1	1	1	1
Silver	1	0	1	1	1	1	1	1	1	1	1	1
Zinc	1	1	1	1	1	1	1	1	1	1	1	1
Phenols	0	1	...	...	...	...	...	...	...	...	...	...
Fluoride	0	1	0	1	1	1	...	...	1	1	1	1

NOTE: Number of successful predictions at 50% (as predicted by a 1) = 60 out of 78. Percent successful predictions = 77%. Number of successful predictions at 95% (as predicted by a 1) = 56 out of 78. Percent successful predictions = 72%.

[a]Foundry A results do not include Lysimeter 2. 50% = median concentration of field leachate samples. 95% = concentration below which 95% of all field leachate samples fall. 0 implies that this parameter not predicted by the batch leaching test but present in field leachate or parameter predicted by batch leaching test but not present in field leachate. 1 implies that this parameter not predicted by batch leaching test and not found in field leachate or this parameter predicted by batch leaching test and found in field leachate.

TABLE 6—*Comparison of average EP (acid) leaching on auger cuttings and field leachate results.*

Leachate	Foundry A[a]		Foundry B		Foundry C		Foundry D		Foundry E		Foundry F	
	50%	95%	50%	95%	50%	95%	50%	95%	50%	95%	50%	95%
Arsenic	1	1	...	...	1	1	1	1	1	1	1	1
Barium	1	1	1	1	1	1	1	1	1	1	1	1
Boron	1	1	1	1	1	1	1	1	1	1	1	1
Cadmium	1	0	1	1	0	1	0	1	0	1	1	0
Chromium	0	1	1	1	0	0	1	0	0	0	0	1
Copper	1	1	1	0	1	1	1	1	1	1	1	0
Iron	1	1	1	1	1	1	1	1	1	1	1	1
Lead	1	0	0	0	1	1	0	1	0	0	1	1
Manganese	1	1	1	1	1	1	1	1	1	1	1	1
Mercury	...	...	...	...	...	...	...	...	...	...	...	...
Selenium	1	1	1	1	1	1	1	1	1	1	1	1
Silver	1	0	1	1	1	1	1	1	1	1	1	1
Zinc	1	1	1	1	1	1	1	1	1	1	1	1
Phenols	1	0	1	1	1	0	1	1	1	1	...	...
Fluoride	1	0	...	...	0	0	1	1	0	0	0	0

NOTE: Number of successful predictions at 50% (as predicted by a 1) = 68 out of 81. Percent successful predictions = 84%. Number of successful predictions at 95% (as predicted by a 1) = 64 out of 81. Percent successful predictions = 79%.

[a]Results for Foundry A do not include Lysimeter 2. 50% = median concentration of field leachate samples. 95% = concentration below which 95% of all field leachate samples fall. 0 implies that this parameter not predicted by the batch leaching test but present in field leachate or parameter predicted by batch leaching test but not present in field leachate. 1 implies that this parameter not predicted by batch leaching test and not found in field leachate or this parameter predicted by batch leaching test and found in field leachate.

TABLE 7—*Quantitative relationship of composite waste EP (acid) leaching and median field leachate concentrations (C values).*

Leachate	Foundry A	Foundry B	Foundry C	Foundry D	Foundry E	Foundry F
Arsenic	1.0[b]	1.0[b]	1.0[b]	1.0[b]	1.0[b]	1.0[b]
Barium	1.0	1.0	1.0	1.0	1.0	1.0
Boron	1.0	1.0	1.0	1.0	1.0	1.0
Cadmium	1.0	0.25	0.10	1.0	0.01	1.0
Chromium	0.06	0.036	0.5	1.0	66.7	1.0
Copper	0.88	1.0[b]	21	14	84	1.0
Iron	0.006	700	0.55	0.10	245	0.01
Lead	1.0[b]	12	1.0[b]	1.0[b]	0.17	1.0[b]
Manganese	0.77	0.13	0.06	0.008	0.06	0.045
Mercury	. . .	. . .	. . .	. . .	. . .	. . .
Selenium	1.0[b]	1.0[b]	1.0[b]	1.0[b]	1.0[b]	1.0[b]
Silver	1.0	1.0	1.0	1.0	1.0	1.0
Zinc	0.18	1.0	0.13	0.07	0.05	0.17
Phenols	0.31	. . .	. . .	. . .	. . .	. . .
Fluoride	0.33	0.11	1.25	0.60	3.3	4.1

NOTE: $C = \dfrac{\text{Field leachate median concentration}}{\text{EP (acid) batch leach test concentration}}$. When any parameter is determined to be less than the analytical detection limit, one half of the analytical detection limit is used as a working value.

[a]Results for Foundry A do not include Lysimeter 2.

[b]Absence of this parameter indicated in both lab and field leachates.

be unrealistic to think a laboratory test could predict field concentrations. Considering values of 1.0 or mixed values above and below 1.0 as reasonable, the EP (acid) test did predict reasonably well arsenic, barium, boron, chromium, iron, lead, selenium, silver, and fluoride. Note that there may be very large errors for a given parameter even though c values were distributed both above and below 1.0. For example, the c value for chromium varied from 0.036 to 66.7 and for iron from 0.006 to 700. Clearly, the EP (acid) test was not accurate in predicting field concentrations even for those parameters for which a consistent bias of too high or too low predictions was absent. Parameters that the EP (acid) test consistently overestimated (c less than 1.0) when the parameters were present were cadmium, manganese, and zinc. The only parameter the EP (acid) test consistently underestimated was copper. The EP (acid) test overestimated the 50% of all samples analyzed as field leachate concentration 27 out of 79 times by factors as large as 170, and underestimated the field leachate concentration 10 out of 79 times by factors as large as 700.

Conclusions

1. Leachate from the unsaturated zone of the six landfills studied by the university had relatively low concentrations with respect to drinking water standards for all contaminants except iron, manganese, and fluoride. Manganese and iron, which are secondary parameters, exceeded the drinking water standards in the majority of leachate samples from all six foundries. Fluoride exceeded the drinking water standard of 1.4 mg/L in the majority of samples from three foundries.
2. The nonhomogeneous nature of foundry wastes and the corresponding landfills can significantly affect leachate quality leading to highly variable water quality depending on the sampling point and the time of sampling.
3. The U.S. EPA EP (acetic acid) extraction procedure was marginally more useful than a similar procedure using deionized water (EP [water]) in predicting the presence or absence of parameters in foundry landfill leachate when run on composite samples of the waste or on auger cuttings taken directly from the landfill.
4. The EP (acid) procedure was not able to predict accurately parameter concentrations in the field leachate samples.
5. Leach tests run on auger samples of waste were more accurate in predicting field leachate composition than leach tests run on raw composite wastes.

Acknowledgment

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Testing Methodologies for Landfill Codisposal of Municipal and Industrial Wastes

REFERENCE: Pohland, F. G. and Gould, J. P., **"Testing Methodologies for Landfill Codisposal of Municipal and Industrial Wastes,"** *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 45–62.

ABSTRACT: The results of a two-year pilot-scale investigation on codisposal of an industrial metal treatment sludge with municipal refuse under the influence of leachate containment and recycle are used to reveal the environmental consequences of heavy metals on such a landfill management practice. Comparisons between landfill simulators with and without varying metal sludge admixtures have provided an opportunity for examination of selected testing methodologies and parameters descriptive of inherent physical-chemical and microbially mediated reactions prevailing throughout the progress of landfill stabilization. Collectively, these analyses were sufficient to determine landfill assimilative capacity in terms of several controlling mechanisms including: potential inhibition of waste stabilization by mobilized heavy metals; precipitation, immobilization, and detoxification of heavy metals by entrapment and filtration; encapsulation and isolation of heavy metals by reaction with carbonates and sulfides; and formation of less toxic metal complexes with humiclike substances and potential for remobilization without transport phase regulation. On the basis of these results, a method for the determination of sludge loadings and their effects at both present and future landfill codisposal sites could be proposed.

KEY WORDS: testing methodologies, landfill codisposal, heavy metals, leachate recycle, assimilative capacity, environmental consequences

In spite of attempts to prohibit disposal of hazardous wastes in municipal landfills, many sanitary landfills receive small but continuous increments of hazardous substances. This codisposal activity has led to environmental impairment, manifested primarily by excursions of leached materials into adjacent surface and ground waters. Although such problems are receiving

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greater attention, many uncertainties remain with respect to the behavior and ultimate fate of hazardous wastes subjected to these land disposal practices.

In recognition of these uncertainties, a two-year pilot-scale research investigation with simulated landfills operated under the influence of leachate containment, collection, and recycle was initiated. This paper presents some of the results of these investigations, including a detailed analysis of leachate characteristics and landfill assimilative capacity as impacted by varying concentrations of heavy metals.

Experimental Procedure

To appropriately detail the temporal and spatial consequences of codisposal on the progress of waste/leachate stabilization, four simulated landfill columns were constructed with operational features as indicated schematically in Fig. 1. Each of the four columns was equipped with a leachate collection and recycle system and either served as a control (Column 1) or test unit (Columns 2, 3, and 4). Leachate recycle was intended to accelerate the progress of landfill stabilization as documented previously [*1*]. The control column received 400 kg of municipal refuse; the tests columns received 400 kg of municipal refuse plus varying quantities of metal plating sludge as characterized in Table 1. Therefore, Columns 2, 3, and 4 were augmented with 33.6, 65.8, and 135.2 kg of metal plating sludge, respectively. These heavy metal loadings, particularly in terms of zinc and chromium, were chosen intentionally to range between levels predicted to be either noninhibitory or inhibitory to the microbially mediated processes of landfill stabilization. This loading strategy was thereby intended to reveal the assimilative capacity of the simulated landfills for the most prevalent heavy metals under the indicated operating conditions.

Operation of the control and test columns commenced with the addition of tap water sufficient to expedite attainment of field capacity and immediate production of leachate for analysis and recycle. Thereafter, moisture was accumulated by incident rainfall. Leachate recycle schedules were determined by experimental phase and associated intent as indicated in Table 2 but were generally at a frequency of one sump volume per week. Hence, the operating history of each simulated landfill included an initial washout period with facile production of leachate, onset of microbially mediated stabilization, a drought/no leachate generation period, a post-drought period, and a terminal leachate production phase. While the chronological details of these phases varied somewhat depending on the specific indicator parameter being examined and the concomitant effects imposed by the heavy metal loadings, the subsequent data presentation generally includes comparisons according to the phases indicated in Table 2, with the exception of the drought period (Phase B′) during which no leachate sampling and analysis were possible. Leachate samples were obtained from each sump after the recycle and associ-

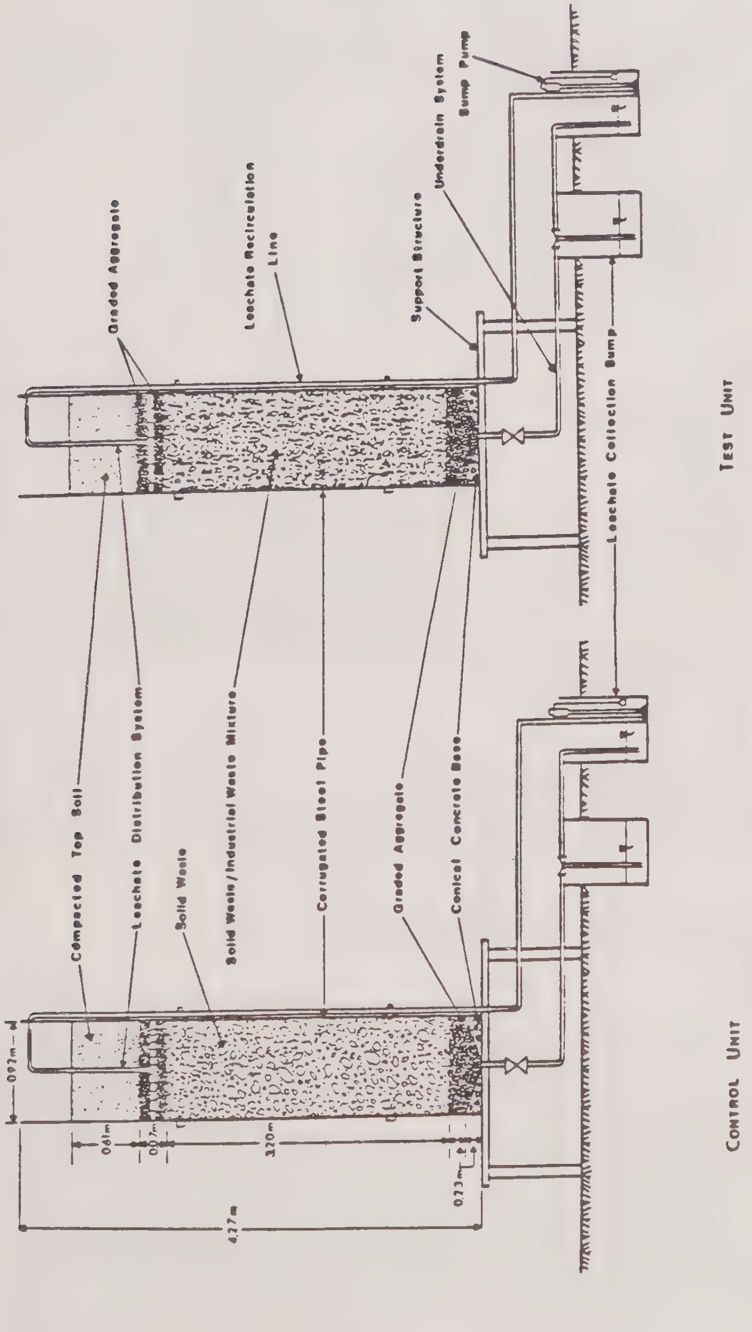


FIG. 1—*Simulated landfill columns used during codisposal investigations.*

TABLE 1—*Characteristics of metal plating sludge used in simulated landfill codisposal investigations.*

Parameter	Analysis[a]
Moisture content, %	84.7
Volatile solids, %	24.6
Zinc (Zn), mg/kg dry	317 000
Chromium (Cr), mg/kg dry	21 000
Nickel (Ni), mg/kg dry	400
Cadmium (Cd), mg/kg dry	13 100
Copper (Cu), mg/kg dry	185
Iron (Fe), mg/kg dry	94 000

[a]Metals determined after acid digestion.

TABLE 2—*Experimental phases for simulated landfill codisposal investigations.*

Experimental Phase	Days[a]	Operational Intent
A	0 to 200	washout or facile production of leachate or both
B	200 to 380	initial microbially mediated stabilization
B′	380 to 480	no leachate production or recycle; period of drought
C	480 to 600	post-drought resumption of leachate production
D	600 to 720	terminal phase of leachate production

[a]Time since loading the simulated landfill columns with wastes.

ated leaching operations had been completed, and indicator parameters and analytical procedures used throughout the experimental period to assess changes in leachate quality were as indicated in Table 3.

Presentation and Discussion of Experimental Results

Preliminary Considerations

Since the admixture of heavy metals with municipal refuse was intended as a superimposition on the normal progress of microbially mediated landfill stabilization, it was considered important to initially establish an understanding of the conditions that generally prevail in the absence of a potential inhibitor. These conditions can be described on the basis of selected parameters as illustrated in Fig. 2 and discussed in detail elsewhere by Pohland et al. [*2–4*]. Indeed, the control column (Column 1) generally exhibited a similar pattern during active leaching in terms of both chemical oxygen demand (COD) and total volatile acids (TVA) analyses. The rapid decline in respective mass concentrations indicated in Fig. 3 after initial washout for Column 1 closely par-

TABLE 3—*Analytical methodology used during simulated landfill codisposal investigations.*

Indicator Parameter	Procedure	Analytical Accuracy
pH	Fisher accument pH meter, Model 144	±0.05
Oxidation reduction potential (ORP), mV E_c	Fisher accument pH meter, Model 144	±5
Conductivity, μS/cm	YSI conductivity bridge, Model 31	±50
Volatile acids total (TVA) and acetic, propionic, butyric isobutyric, valeric; mg/L as acetic acid	Perkin-Elmer Sigma 1 gas chromatographic system	±5%
Total carbon (TC), mg/L	Beckman total carbon analyzer, Model 915	±5%
Total inorganic carbon (TIC), mg/L	Beckman total carbon analyzer, Model 915	±5%
Total organic carbon (TOC), mg/L	Beckman total carbon analyzer, Model 915	±5%
Ammonia nitrogen, mg/L as N	Technicon auto analyzer	±10%
Total kjeldahl nitrogen (TKN), mg/L as N	Technicon auto analyzer	±10%
Total metals, mg/L Fe, Ni, Mn, Cr, Cd, Mg, Cu Na, K, Ca, Zn, Pb	Perkin-Elmer atomic absorption spectrophotometer, Model 303	±5%
Orthophosphate, mg/L as $PO_4^{\equiv}$	Technicon auto analyzer	±10%
Chemical oxygen demand (COD) [6], mg/L		±5%
5-Day biochemical oxygen demand (BOD_5) [6], mg/L		±10%
Total solids (TS) [6], mg/L		±10%
Total volatile solids (TVS) [6], mg/L		±15%
Suspended solids (SS) [6], mg/L		±10%
Volatile suspended solids (VSS) [6], mg/L		±15%
Sulfide [6], mg/L as $S^{=}$		±10%
Chloride [6], mg/L		±5%
Total Alkalinity [6], mg/L as $CaCO_3$		±5%
Carbohydrates [6]	phenol-sulfuric acid method	±20%
Aromatic hydroxyls (ArOH) [6]	tungstophosphoric-molybdophosphoric acid method	±10%
Carboxylic acids [6]	ferric-hydroxmate method	±20%

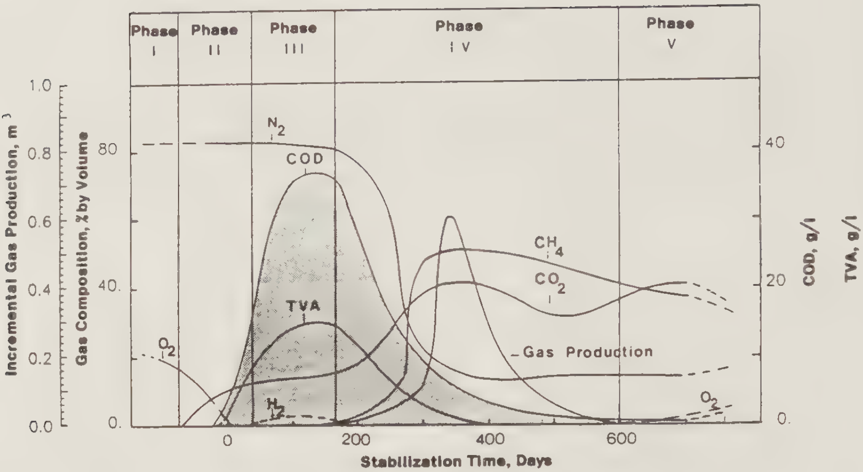


FIG. 2—*Temporal trends in leachate characteristics during the phases of landfill stabilization; Phase I: initial adjustment; Phase II: transition; Phase III: acid formation; Phase IV: methane fermentation; and Phase V: final maturation.*

allels such a conversion process with leachate recycle, and although confirmation based on gas production and quality was not possible, the control column data were considered representative of normal landfill stabilization events, and any deviations noted between them and those for the test columns could be easily detected by simple comparison. Indeed, as indicated in Fig. 3, a rather significant difference in COD and TVA was indicated, particularly with leachate samples from Columns 3 and 4. This suggested an interruption in the normal progress of microbially mediated landfill stabilization.

Effects of Metal Loadings on Landfill Stabilization

The differences in measured levels of COD and TVA in the test column leachates during the four operational phases best illustrate the effects of the heavy metal loadings. Using leachate COD as an overall indicator of potentially available substrates for microbial conversion, the temporal variations indicated in Fig. 3 reflected a relatively normal pattern of rapid initial washout/microbially mediated stabilization to a constant level after about 200 days for the control column. This constant level was then maintained essentially unchanged for the duration of the study, apparently uninfluenced by the period of drought (Phase B′). The leachate from the column with the lowest metal sludge loading (Column 2) demonstrated a similar pattern except for an increase in COD levels immediately before the drought period and again, but to a lesser extent, toward the termination of the experimental stud-

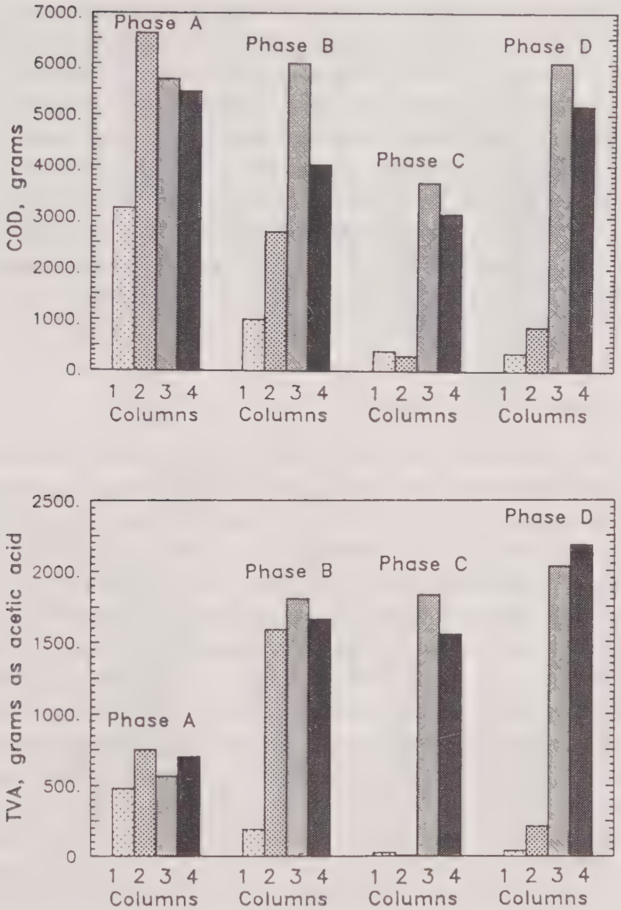


FIG. 3—*Average mass concentrations of leachate COD and TVA during the experimental phases.*

ies. In contrast, leachate COD levels for Columns 3 and 4, although similar to each other, exhibited significant increases before the drought period, decreased precipitously during the drought period, and then increased to a peak level.

Collectively, these variations strongly suggested an interference with normal microbially mediated landfill stabilization processes. In addition, this inhibition appeared to manifest itself in a cyclic fashion, resulting in alternating periods of toxicity or inhibition and subsequent acclimation with time, particularly at higher metal sludge loadings. (Complementary biochemical oxygen demand [BOD_5] data confirmed the COD observations, again emphasizing the capacity to adapt to certain loading levels of heavy metals. In addition,

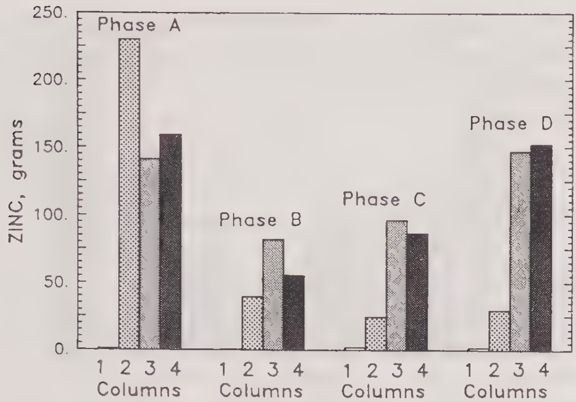
the inherent degradability of the organic compounds present in the leachate and measured by the BOD_5 apparently was not impaired once the leachate became more dilute and the influence of the heavy metals was reduced.) Within an operational perspective, this suggests that leachate generated in localized regions of high heavy metal concentration in a conventional landfill will be ameanable to conversion by uninhibited biological communities located in other portions of the landfill as migration occurs. Therefore, in terms of assimilative capacity, heavy metal loadings at 33.6 kg to Column 2 apparently could be accommodated; 65.8 and 135.1 kg to Columns 3 and 4, respectively, exceeded the adaptation threshold and definite inhibitory influences resulted.

Specific Behavior of Heavy Metals

Because zinc (Zn) and cadmium (Cd) were the most prevalent heavy metals extracted from the sludge added to the test units, they were logical candidates to examine in terms of impacts of heavy metal loadings on overall landfill stabilization. Average leachate levels for these two heavy metals during the four operational phases outlined previously are shown in Fig. 4. Although leachate zinc and cadmium levels were almost undetectable for Column 1, an initially rapid washout of readily mobilized metals followed by a significant degree of fixation occurred in Column 2 and to a lesser extent in Columns 3 and 4. This initial decrease was enhanced by the early onset of anaerobic reducing conditions and the production of metal precipitating sulfides. Negative redox potential (ORP) values, even during the drought (no leachate) period, confirmed these reducing conditions, which restricted the release and possible mobilization of heavy metals. However, in the final stages of the investigations (Phase D), leachate metal concentrations increased, particularly for Columns 3 and 4, thereby indicating the possibility of remobilization.

In searching for an explanation for the apparent mobility of the heavy metals during the later stages of the research investigation, it was considered plausible that other leachate constituents, such as the humiclike substances, may have contributed. To assess this possibility, leachate samples were subjected to additional analyses for hydroxylated aromatic (ArOH) compounds that are considered related to the moderate to high molecular weight compounds similar to, if not identical with, humic substances commonly found in many natural environments. These substances are known complexing agents and would be available as natural inputs or as products of hydrolysis and microbial conversion of refuse materials. Therefore, the availability of ArOH during these investigations was likely also linked to the phases of landfill stabilization.

The variations in mass of ArOH in the leachates from the landfill columns as a function of experimental phase are presented in Fig. 5. The ArOH levels determined for Columns 1 and 2 are very similar, with an initial rapid wash-



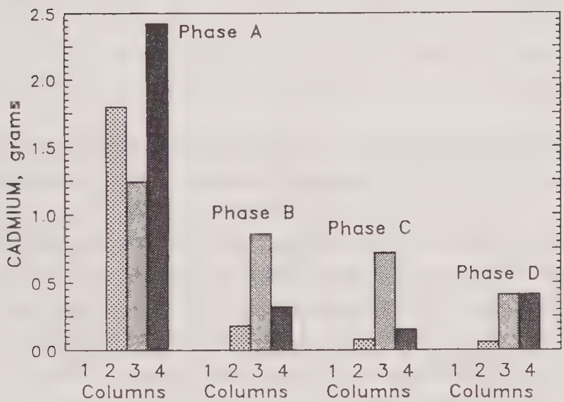


FIG. 4—*Average mass concentrations of leachate zinc and cadmium during the experimental phases.*

out followed by relative stability in mass concentrations. Moreover, the interruption in leachate production during the drought period (Phase B′) indicated little influence on measured amounts, although some slight retardation of production may have occurred in Column 2. In addition, the stabilized levels in either case were equivalent to concentrations of only 10 to 20 mg/L, thereby indicating that the source waste material decomposed very slowly to release humiclike substances into the leachate.

In contrast, leachate ArOH levels remained higher for Columns 3 and 4 after initial washout. This may have been due to direct inhibition of microbially mediated conversion processes by the higher heavy metal sludge loadings or interaction between the ArOH and heavy metals, thereby reducing their susceptibility to degradation. In addition, examination of Fig. 5 indi-

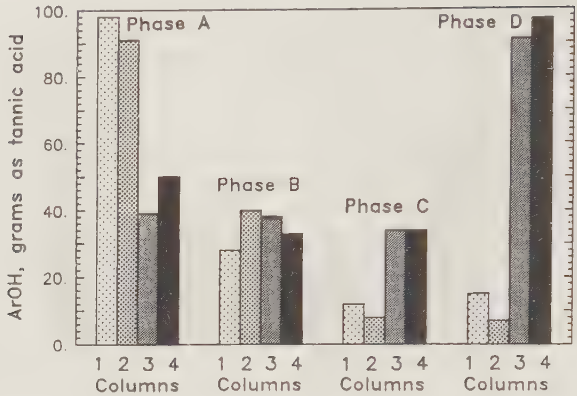


FIG. 5—*Average mass concentrations of leachate aromatic hydroxyl constituents during the experimental phases.*

cates that initial ArOH levels in the leachates decreased relatively smoothly with increasing rather than decreasing sludge loadings or opposite to what may have been otherwise expected. Recognizing that the metal sludge was added to the columns as a semi-solid metal hydroxide, this behavior was probably attributable to the potential for sorbtive interaction between the humic substances/heavy metal complexes, resulting in fixation of a portion of the ArOH on the solid phase hydroxide. The increased contact between the leachate and the solid phase materials arising from leachate recycle probably facilitated this fixation process.

The sharp increase in ArOH levels in the leachates from Columns 3 and 4 during the later stages of the investigations suggests a combination of inhibition of the microbial decomposition of ArOH, a similar enhancement of ArOH release as more refractory waste organics were metabolized, and the possible displacement of materials bound to the metal sludge by sulfides. The abundant reservoir of sulfate contributed with the sludge, its conversion to sulfides under reducing conditions, and the preference of heavy metals for sulfides over other ligands collectively support the plausibility of this hypothesis.

Factors Controlling Heavy Metal Solubility

Since one of the primary goals of the research investigations was to explore the behavior and fate of heavy metals codisposed with solid waste, an understanding of factors influencing and controlling heavy metal solubility was considered paramount. As has been discussed in detail elsewhere [5], pH, ORP, and complexing agents (as well as ionic strength) tend to determine the relative solubility of all leachate constituents. In general, metal solubility will

increase as pH decreases, and the progress of landfill stabilization through acid formation and consumption (Fig. 1) will, therefore, significantly influence heavy metal behavior as the pH of the reaction medium changes. In these investigations, except when initial washout and leachate production prevailed (Phase A; pH increased from 5.5 to 7.0), the pH was near neutral either because of microbial conversion of the organic acids (Column 1) or, more likely, interaction and neutralization with the basic hydroxide sludge (Columns 2, 3, and 4).

With regard to ORP, the chemical environment of a landfill is typically reducing because of the microbially mediated oxidation-reduction reactions and limited access to atmospheric oxygen. This condition will impact heavy metal mobility either by favoring reduced over oxidized species, for example, Fe^{+2}/Fe^{+3}, or by encouraging formation of precipitating agents such as sulfides, for example, $SO_4^{-2} \rightarrow S^{-2}$. On the other hand, while leachates may contain sulfides (as well as CO_3^{-2} and possibly OH^-), organic complexing ligands may also be present to compete with the precipitants and concomitantly increase solubility of heavy metals with the release of the precipitating anion.

In general, pH will determine the relative distribution of those precipitating anions most commonly available in leachates, that is, sulfide, carbonate, and hydroxide, as indicated by the pH-pC diagram for zinc included in Fig. 6. Moreover, the negative ORP normally prevailing within the landfill environment will help determine the speciation of several of these leachate constituents. Since the production of sulfide under reducing conditions has been regarded as the major mechanism controlling most heavy metal mobility caused by the precipitation of very sparingly soluble metal sulfides (Fig. 7), the dominance of this mode of metal fixation in landfills is underscored as is further emphasized by the E_c-pH diagram of Fig. 8 for the $SO_4^{-2}/S(s)/S^{-2}$ redox system. The excess reservoir of sulfates available in the metal sludge added to the test columns, coupled with its release as sulfides within the associated leachates (Fig. 9) under persistent reducing conditions (ORP < -200 mV), further attests to the importance of this removal mechanism.

The associated role of complexation in complicated matrices, such as leachates, involves considerable uncertainty. By converting sparingly soluble salts to soluble complexes, various complexing agents can counteract the action of precipitant ions and thus increase the solubility of heavy metals. Previously reported investigations have discounted complexation between even the most abundant inorganic ligands (chloride and sulfate) and any of the metals common to the sludges used during these investigations [5]. Likewise, other identified organic species, with the exception of the hydroxylated aromatic (ArOH) compounds as previously discussed, are simply too weak as ligands to be of substantial influence in heavy metal solubilization. Therefore, the ArOH compounds were considered of pivotal importance in the control of heavy metal behavior during these investigations; similar control would be expected to be operative at most codisposal sites.

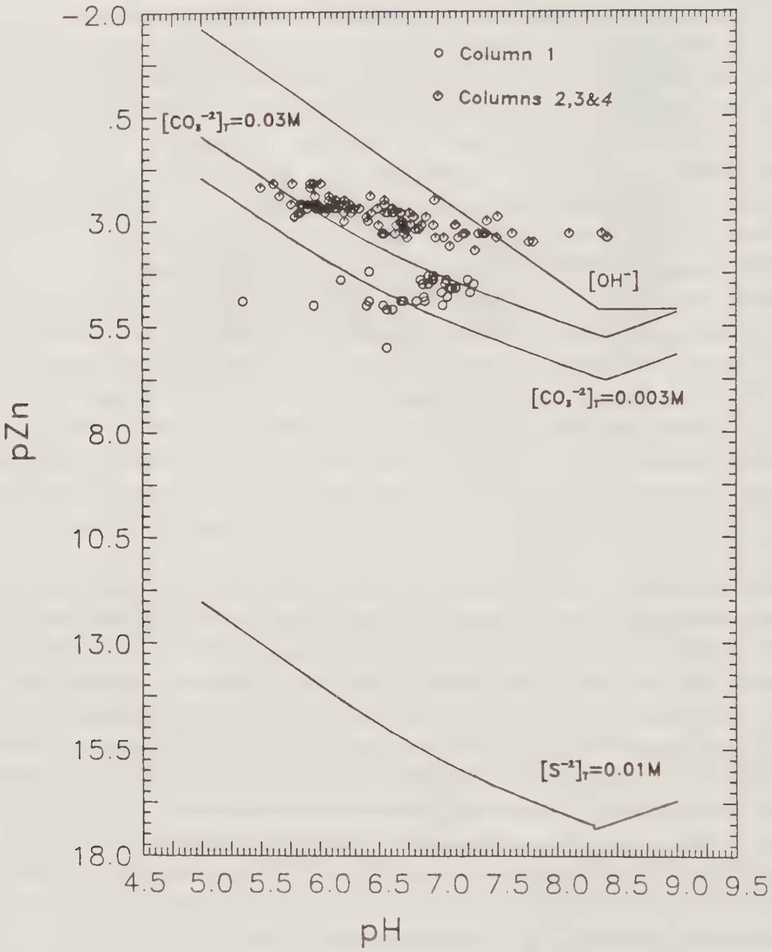


FIG. 6—*pH-pC diagram for zinc solubility under hydroxide, carbonate, and sulfide control.*

Although routine monitoring for leachate cadmium, chromium, copper, iron, manganese, nickel, and zinc was conducted throughout the investigations, zinc, cadmium, and nickel were the only elements originally present in the industrial sludge that were detected with consistency. Moreover, since zinc was the major heavy metal sludge constituent, an initial examination of its solubility behavior was considered appropriate. As presented previously (Fig. 6), the major potential solubility control is associated with sulfide as the precipitant; carbonates would be the next most effective, and hydroxides would be the least likely to form. By also plotting measured pZn versus pH data on Fig. 6, the three test columns exhibited little difference in plotting

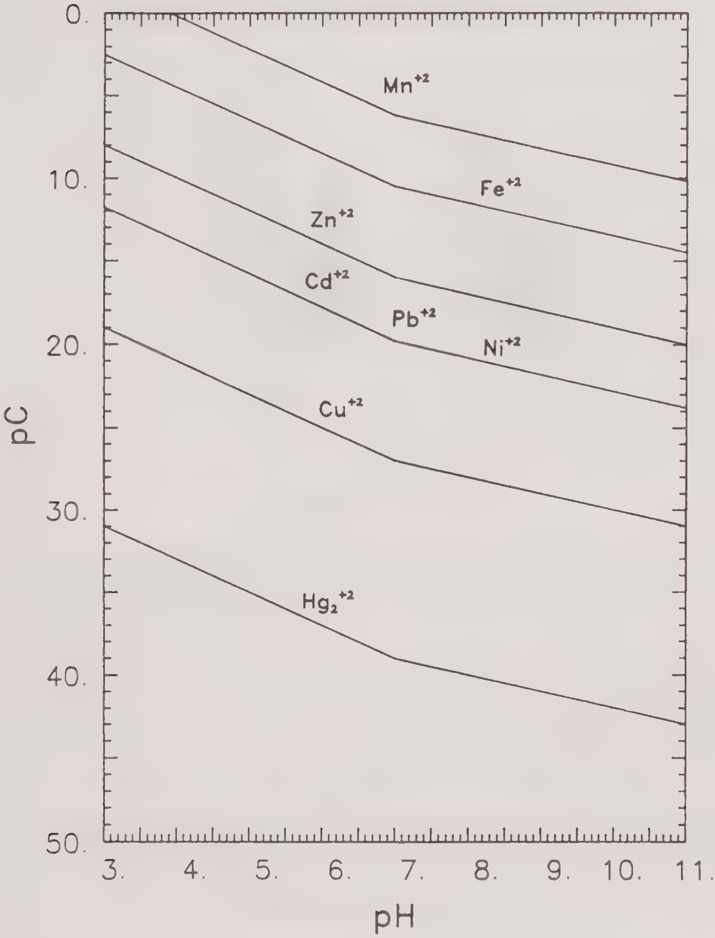


FIG. 7—*Solubility of selected heavy metals under sulfide control (sulfide* C_t *= 0.02* M*).*

position, thereby suggesting that all three were at apparent saturation in terms of zinc and the leachate environment (a consequence enhanced by the opportunity for more intimate contact and resultant more complete equilibration with leachate recycle). However, while these data tended to cluster mainly between the carbonate and hydroxide solubility curves, those at high pH exceeded even the solubility limits where hydroxide solubility would be presumed to control. Therefore, whatever solid phase was controlling zinc solubility, there was apparently superimposed upon this system some factor that served to increase solubility. The most logical explanation was considered to be the presence of some other complexing agent.

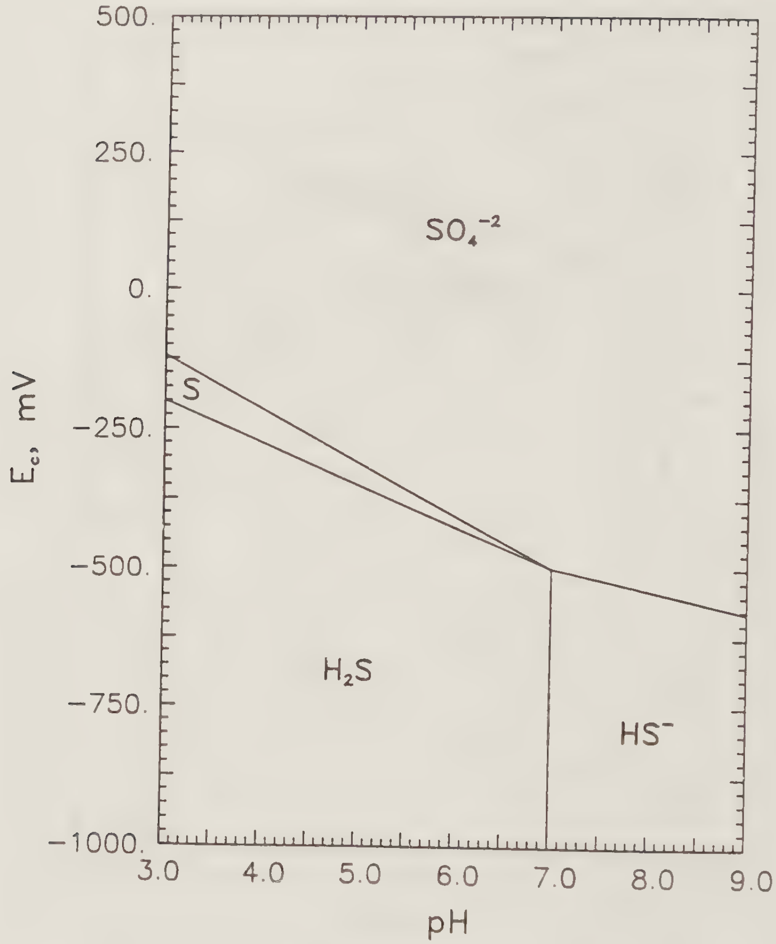


FIG. 8—E_c-*pH diagram for* $SO_4^{-2}/S(s)/S^{-2}$ *redox system.*

As suggested previously, the most likely complexing agents available in leachates in relative abundance are the moderate to high molecular weight phenolic compounds generally referred to as humic substances. Analysis of the hydroxylated aromatic (ArOH) compound groups provided an effective measure of these substances. From Fig. 5, measured ArOH for all landfill columns decreased rapidly to essentially constant levels. Thereafter, these levels were maintained in the control (Column 1) and test column with the lowest sludge loading (Column 2), whereas they increased in the leachates from Columns 3 and 4. This difference also reflected the fluctuating nature of

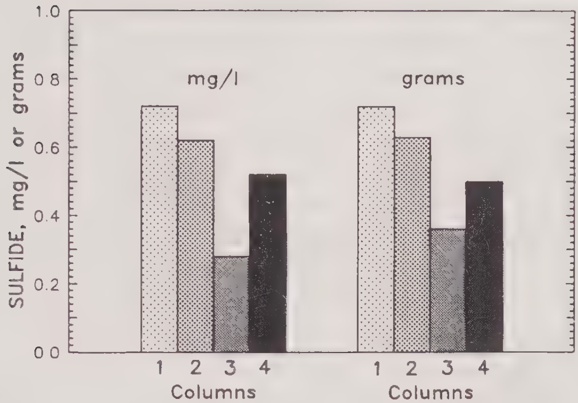


FIG. 9—*Average content of leachate sulfide throughout experimental phases.*

the inherent stabilization processes, that is, a cyclic sequence of microbial inhibition followed by acclimation, particularly in the test columns with the higher metal sludge loadings.

The suggested relationship between ArOH and soluble heavy metal concentrations from all columns is better illustrated in Fig. 10 for zinc and cadmium. A marked positive correlation between aromatic hydroxyl and zinc solubility strongly supports the concept that humic substances, as quantified by the ArOH analysis, played a major role in leachate zinc solubilities. A similarly positive correlation for cadmium was also obtained, although more scatter was observed than in the case of zinc. This scatter was probably attributable in part to the relatively low (0 to 5 mg/L) dissolved cadmium concentrations; zinc concentrations were two orders of magnitude higher.

Summary and Conclusions

The presence of industrial metal plating sludges during landfill disposal of municipal refuse increased the concentrations of leachate zinc and cadmium as microbially mediated stabilization progressed. Following an early period of washout and rapid mobilization of these heavy metals, a balance between processes of metal fixation and mobilization led to reduced and relatively stable leachate metal concentrations. Leachate recycle increased contact opportunity with the sludge solids and accelerated reactions descriptive of the overall stabilization process. Experimental evidence, reinforced by visual examination, indicated that the metal hydroxides in the sludge matrix interacted with the soluble leachate constituents and led to an encapsulation of the sludge particles in a protective layer of very sparingly soluble sulfides and

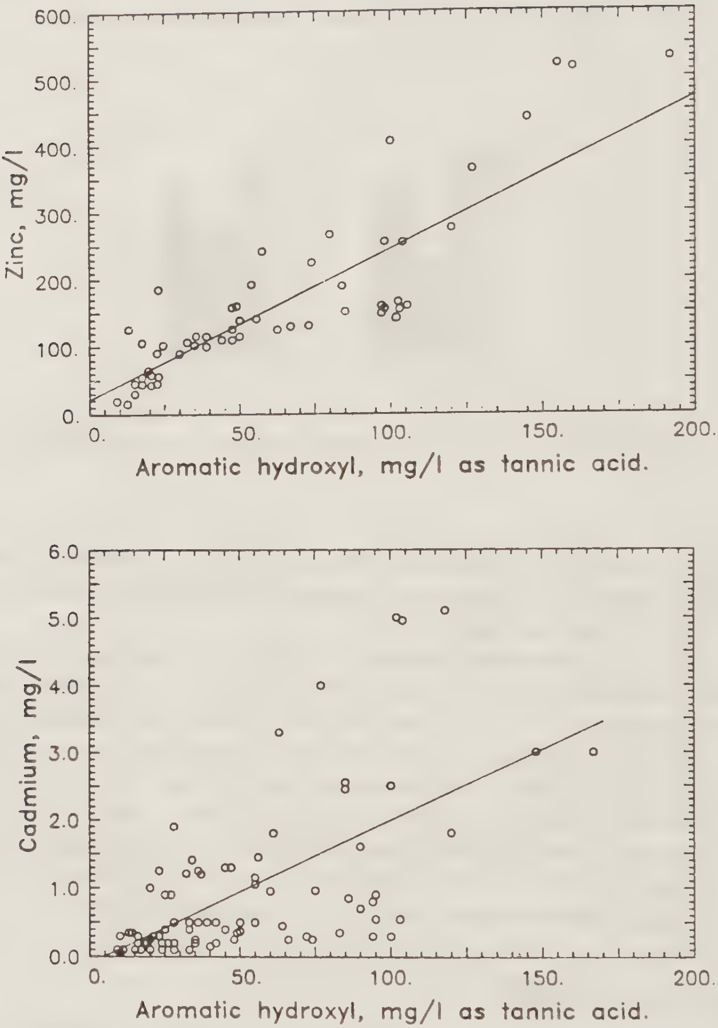


FIG. 10—*Relationship between concentrations of leachate aromatic hydroxyl concentrations and zinc and cadmium during experimental phases.*

carbonates. This phenomenon markedly reduced the opportunity for further leaching and mobility of heavy metals from the sludge reservoir and moderated the otherwise toxic influence of heavy metals on the microbially mediated processes of refuse stabilization.

Although higher metal sludge loadings led to distinct inhibitory effects, the simulated landfill systems displayed a significant ability to adjust to this impact below a certain threshold or limiting assimilative capacity. As long as the admixture loadings were below this level, inherent mechanisms of reaction

were sufficient to compensate for the inhibitory properties of the heavy metals, although this accommodation tended to proceed in a cyclic fashion.

In addition to those mechanisms responsible for immobilization of the heavy metals, namely, precipitation or sorption or both, offsetting and competing mobilizing mechanisms were also operative. The strong correlation between levels of dissolved zinc and cadmium and the hydroxylated aromatic components of the leachate suggested metal-humic substance complexes capable of mobilizing or remobilizing the heavy metals and perhaps also diminishing their otherwise inhibitory consequences. Therefore, when considered collectively, landfill assimilative capacity for heavy metals involves a combination of mobilization by leaching particularly under acid conditions, sulfide precipitation, and immobilization enhanced by reducing conditions and filtration during leachate recycle, encapsulation of metal hydroxide sludge particles by sulfides and carbonates, and mobilization or remobilization through formation of metal complexes with humic substances.

In summary, it has been demonstrated that

1. Heavy metal sludge could be effectively assimilated within a landfill when codisposed with municipal refuse in a ratio of 0.077 kg of sludge per 1 kg of admixed refuse and exposed to the influences of leachate containment and recycle. At higher sludge loadings, inhibitory effects were detected, which interrupted the normal progress of microbially mediated landfill stabilization.

2. Encapsulation of the metal hydroxide sludge solids, originally added with the refuse to the simulated landfills, by a protective layer of sparingly soluble sulfides and carbonates provided a major assimilative mechanism, while aromatic hydroxyl substances acted to mobilize the heavy metals through the mechanism of complexation, the toxicity of the mobilized metals may have been substantially reduced by this complexation.

3. Leachate recycle enhanced contact and homogenity of reaction opportunity with a resultant decrease in parametric variability and accelerated attainment of equilibrated conditions with respect to the inherent chemical and biological processes of waste stabilization. Such control over the major transport phase (leachate) provides new opportunities for evaluation, design, and control of both existing and future codisposal sites.

4. Since the ultimate environmental impact of landfill codisposal practices, even at small generator quantities, is linked to the intrinsic nature and manner by which admixed materials are combined with municipal refuse in a particular landfill setting, additional investigations on the various categories, and possible combinations of refuse and hazardous wastes need to be conducted for both diagnostic and design purposes.

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An Approach for Evaluating Long-Term Leachability from Measurement of Intrinsic Waste Properties

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ABSTRACT: This paper presents a radically new approach for evaluating hazardous waste leachability. In the past, leachability has been measured through conductance of laboratory leaching tests, either batch or column, using experimental conditions that attempt to simulate field conditions. An approach is proposed in which measured intrinsic properties of a waste are used in mathematical models to infer the long-term leachability.

To provide background information, laboratory leaching tests are reviewed with emphasis on interpretation of the results. It is argued that results of bench-scale tests are difficult to scale up to field disposal conditions and that they do not lend themselves to extrapolation over time.

Leaching from wastes takes place via solubilization of contaminants inside the matrix and transport through the matrix pore system to the surrounding aqueous solution. Intrinsic properties that determine leaching rates can be categorized as chemical or transport phenomenon. Chemical properties include those factors that determine a contaminant's solubility, for example, chemical speciation, precipitation, adsorption, kinetics of reaction, buffering capacity, and so forth. Transport properties include structure of the pore system, factors affecting diffusion of ions in the pores, and hydraulic conductivity. Laboratory methods to measure these properties are briefly described.

A mathematical model, developed to predict leaching of toxic metals from solidified wastes under acidic conditions, is described. The model uses measured properties of wastes to predict leaching rates under a variety of conditions. Verification experiments are presented and the merits and limitations of the model for long-term predictions are discussed.

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Evaluation of the leaching potential of contaminants is the most difficult problem associated with land disposal of hazardous solid wastes. Contaminant leaching is affected by many factors, including the physical, chemical, and engineering properties of the waste and the leaching environment. Wastes contain different contaminants that will leach at various rates depending on the chemical environment established in the landfill and on the leachant characteristics and its hydraulic regime. The complexity of these phenomena has led to the situation where several factors are lumped together, and the leaching potential is evaluated by conducting a laboratory leaching test.

Laboratory leaching tests, conducted either in batch mode or in a small column over short periods of time, generate results in terms of contaminant concentration in the leachate. Leaching tests have been included in regulations, and performance criteria have been set in terms of maximum allowable concentrations of specific contaminants. A considerable amount of effort has been expended to make those tests rapid, inexpensive, and reproducible. In the process, the emphasis has been shifted from "measuring a hazardous property of a waste" to "meeting the performance criteria of the test."

The use of standard tests and performance criteria, while being practical in a regulatory framework, does not answer the fundamental concerns associated with land disposal of hazardous wastes:

1. How will different field environmental conditions affect leaching rates?
2. What are the long-term trends in leachability?

These questions can be addressed by considering leaching from a mechanistic point of view. In this approach, a waste is characterized for its intrinsic physical and chemical properties, independent of any particular field leaching environment. This information alone will often be sufficient to evaluate the suitability of a given leaching environment. It can also be used in mechanistic leaching models to infer the long-term leachability under specific leaching conditions. This approach has been used to evaluate the leachability of cement-based waste forms.

In this paper, the mass transport and chemical principles by which leaching takes place will be reviewed, and the limitations associated with measuring leachability in the laboratory will be noted. Intrinsic waste properties that are related to leachability will then be surveyed, and methods that can be used to measure them will be mentioned. Finally, a mechanistic leaching model will be presented, and the way instrinsic waste properties are utilized by the model will be illustrated.

A Mechanistic Approach to Leachability Evaluation

A solid waste can be generally described as a porous solid partially saturated with water. It consists of several solid phases, a liquid phase (pore solution), and air voids. Before being contacted with a leachant solution, the different chemical species in the solid phases and in the pore solution are in a state of chemical equilibrium. Upon contact, the difference in chemical potential of species in the aqueous and solid phases leads to fluxes of mass between the surface of the solid and the aqueous leaching solution. The surface exchanges create concentration gradients inducing bulk diffusion within the pore solution of the waste matrix. Species from the solid and from the leachant may also interact to form new species both in the aqueous solution and in the solid. These principles apply to species initially present in the leachant and in the solid.

Several transport mechanisms and chemical reactions that would be part of a comprehensive mechanistic leaching model are presented in Fig. 1. This conceptual model represents, in a unidimensional geometry, the interactions and transport of several chemical species C_i as a function of distance z and time t. The superscripts represent concentrations in the bulk of the waste matrix (b), in the leachant (l), and in the aqueous solution (w). Leachant is used to describe the leaching liquid before any interaction with the waste while aqueous solution refers to the liquid at the interface.

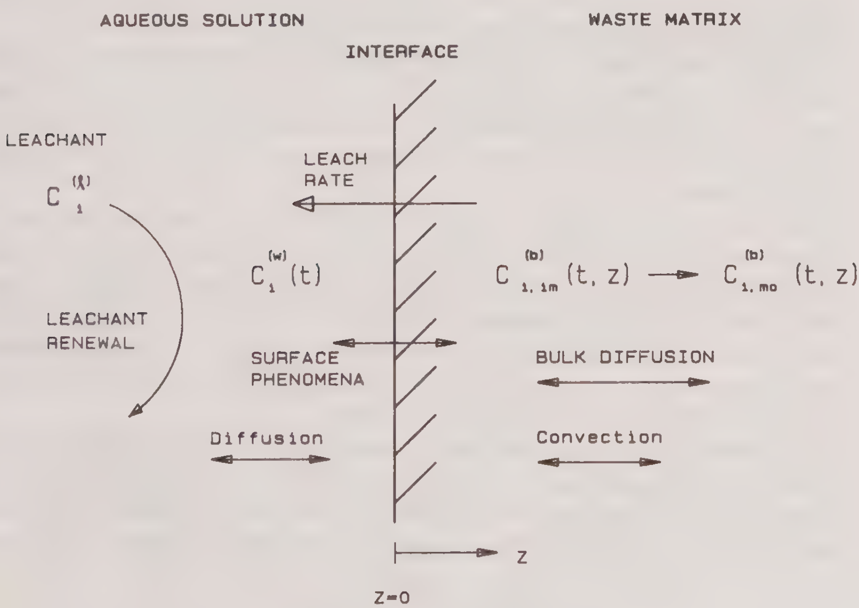

FIG. 1—*Conceptual leaching model.*

The chemical species of interest to leaching are initially present in the waste matrix in an immobile form ($C_{i,\mathrm{im}}^{(b)}$) or in a mobile form, that is, in solution in the pore solution ($C_{i,\mathrm{mo}}^{(b)}$). The immobile form that may be either precipitated or adsorbed on the matrix is subject to mobilization if the local equilibrium is disrupted as a result of the mobile form being transported by diffusion or convection.

Mobilization can be instantaneous (that is, the distribution between the mobile and immobile forms can be described using equilibrium chemistry) or rate limited (in which case it must be described using kinetic expressions). Chemical species of significance to leaching can also be present in the leachant; species such as H^+ or organic complexing agents, represented by $C_i^{(l)}$ might be involved in surface phenomena or even diffuse into the matrix to enhance the mobilization reactions.

Finally, the concentration of chemical species at the interface, which determines the driving force for exchange, is represented by $C_i^{(w)}$.

Leaching is normally expressed as a leach rate, which is defined as the net mass of species "i" crossing the waste-aqueous solution interface per unit area per unit time

$$L_i(t) \equiv \left[\frac{\text{mass}}{\text{area} \cdot \text{time}}\right]$$

$L_i(t)$, which is positive for species leaving the solid, is normally expressed based on the geometrical surface area of the waste.

From a mass transport point of view, leaching can take place via two mechanisms: convection and interface transfer. Convection refers to the bulk movement of the leaching solution. It can be important for more permeable wastes subjected to high hydraulic gradients where the leachant flows through the waste mass.

Interface transfer, which can be subjected to a mass transfer resistance, takes place as a result of the different chemical potential of species on the solid's surface and in the aqueous solution. If the chemical components that constitute the bulk of the matrix are soluble themselves in the leachant, then contaminants are released at the rate at which the matrix undergoes dissolution. Concentration gradients also force species to diffuse within the pore system of the matrix, both inward and outward.

The hydraulic regime of the aqueous solution has a profound effect on the system since it establishes the interface concentrations and by extension, the driving forces for leaching. The leachant velocity v can be defined as the volume of leachant contacted with the waste per unit surface area per time, that is

$$v \equiv \left[\frac{\text{volume}}{\text{area} \cdot \text{time}}\right] \equiv \left[\frac{\text{distance}}{\text{time}}\right]$$

The effect of the hydraulic regime of the leachant on the leach rate can be visualized by considering the dependency of a time invariant leach rate as a function of the leachant velocity (Fig. 2). The hypothesis that led to the development of this curve has been discussed elsewhere [*1*].

The slope of the curve in Fig. 2 has concentration units. The curve has two asymptotical limits where the slope can be interpreted as the concentration of the leached species near the interface. Limit 1, the maximum leach rate, is reached when the leachant velocity tends toward infinity. Under such flow conditions, there is no accumulation of leached species in the leachate (the slope of the curve tends toward zero) and the leaching driving forces are maximum. Limit 2 represents the saturation concentration of a species under the given leaching conditions. This limit can be approached for tests conducted under a sufficiently low leachant velocity.

Leaching is a dynamic phenomenon, changing with time. Leaching can be limited by a number of rate controlling mechanisms. Among the most significant are (1) the accumulation of species in the aqueous solution near the interface, (2) the limited supply of a chemical species in the leachant (such as H^+), which are responsible for contaminant mobilization, (3) bulk diffusion within the matrix (that is, from the interface to a reaction front), and (4) slow mobilizing chemical reaction (for example, redox reaction).

Limitations of Laboratory Leaching Tests

Attempts to correlate the results of laboratory leaching tests with field data have not proved successful [*2-4*]. Several factors can be responsible for this.

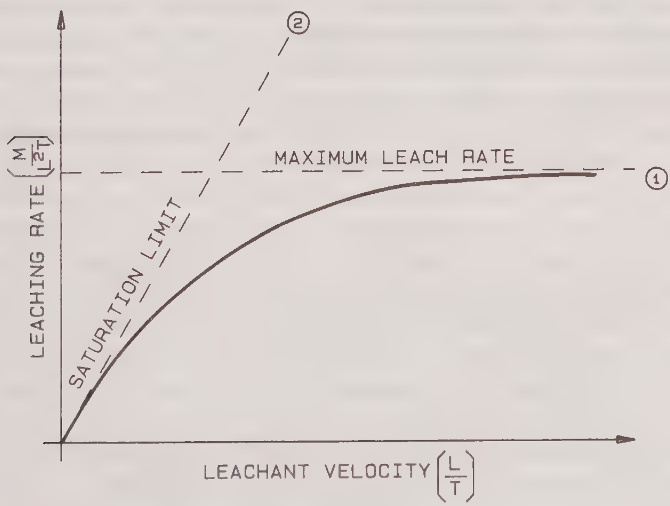

FIG. 2—*Effect of the leachant velocity on the leaching rate.*

The leachants used in laboratory leaching tests are normally more aggressive than their field counterparts because they are prepared by adding high concentrations of chemicals (for example, acids and complexing agents) to distilled water [*5*–*7*]. In addition, distilled water lacks the background concentration of common chemical elements found in ground water, and therefore forces higher dissolution rates of the waste matrix. Leaching in the field is often rate limited while equilibrium conditions are commonly reached in laboratory tests, particularly in batch tests [*8*]. Mendel et al. [*9*] reported the results of identical leaching tests performed on various waste forms and naturally occurring materials. They observed that several naturally occurring minerals showed higher leach rates than the waste forms tested and concluded:

> "Clearly such leach rates do not prevail in nature. If they did, the land masses would have dissolved away long ago. The mere fact of persistence of the natural materials demonstrates that the short-term leach rates measured in the laboratory do not apply to long-term conditions. There are rate-inhibiting processes in the natural surroundings that protect natural materials and that may also slow the leaching of waste forms.

Laboratory leaching procedures that attempt to simulate field conditions are not appropriate to predict long-term leachability. Even if a leaching test existed that would perfectly simulate field conditions, it would only represent a time period equivalent to the test duration.

Chemical equilibrium between the liquid and solid phases is normally assumed to be reached in batch leaching procedures. Once equilibrium has been reached, there is no net transfer of contaminants from the solid to the liquid. The leach rates are equal to zero. The results of these tests indicate the solubility or availability of the contaminants under the prevailing batch leaching conditions. This information is important since contaminants can only be transported (that is, leached) in their soluble forms. However, the concentrations measured do not provide kinetic information, and therefore they can not be interpreted in terms of time. If chemical equilibrium is not approached in a batch test, then the wrong tool was used since the results represent only one point of a process that changes in time.

Batch leaching tests as opposed to column tests are mostly used to quickly evaluate the potential leachability of hazardous wastes. The selection of test conditions and their impact on the results have received much attention in the literature [*6,8,10*]. Some observations can be made if it is assumed that chemical equilibrium is approached or reached during the test. In this case, the particle size of the waste, the duration of the test, or the method of agitation should have little if any effect on the results. A finely crushed waste, in particular, does not result in a more aggressive test but simply speeds up attainment of equilibrium. The characteristics of the leachant are important in as much as through interaction with the waste, the leachant establishes the environmental conditions under which the concentrations of soluble contaminants will be measured. For example, reporting the results of a "batch test conducted at pH = 5 (pH of the leachant) is meaningless if the pH of the leachate at the end of the test has risen to 10.

The effect of the liquid-to-solid ratio on the results of a batch test vary with the type of leachant [*11*]. If the leachant is mild, the leaching environment is established by the waste and one of two boundary conditions exist:

1. Sufficient contaminant is available in the waste to saturate the leachate at all ratios. Increasing the liquid-to-solid ratio will increase the total mass release but will not change the concentration.
2. The amount of contaminant available for dissolution is limited. Increasing the liquid-to-solid ratio will result in dilution (decreased concentration) while the mass release will be constant.

If the leachant is aggressive (for example, low pH) it will control the leaching environment. In this case, increasing the liquid-to-solid ratio will change the leaching environment and no inference can be made on the effect of the change on measured concentrations.

Waste Form Intrinsic Properties Related to Leachability

Several waste stabilization/solidification processes, based on the addition of a hydraulic binder, are listed in Table 1. Portland cement is most frequently used but other types have also been used, such as aluminous cement, pozzolanic cement, or gypsum cement. Cement-based processes are well suited to the treatment of aqueous wastes since cement needs water for hydration. The hydration of portland cement calcium-silicates also creates an alkaline environment (0.30 g of calcium hydroxide ($Ca(OH)_2$) produced per gram of fully hydrated cement) suitable to the insolubilization of toxic metals.

Measurement of the intrinsic properties of a waste can be done without having to make assumptions about the field disposal conditions. These measurements, however, provide valuable information on the potential leachability in various environments. Intrinsic properties can be categorized as chemical or physical properties.

TABLE 1—*Stabilization/solidification systems for hazardous wastes based on cement* [12].

Cement
Lime-cement
Pozzolan-lime
Pozzolan-cement
Clay-cement
Soluble silicate-cement
Lime/cement kiln dust
Slag-cement/lime
Gypsum

Physical Properties

Physical properties are indicative of the way water can be contacted with the waste; a cement-based waste form, depending on the additives used and their dosage, can be a granular soil-like material or a monolythic concrete-like mass [*13*]. A solidification operation increases the volume of an aqueous waste from about 25 to 150% depending on the type of waste, its water content, and the additives used [*14*]. The solidified waste matrices have porosities typically varying from 25 to 75% [*15,16*], and the pores are only partially saturated with water. Permeability coefficients are comparable to those of clay, ranging from 10^{-7} to 10^{-9} m/s [*15,16*]. These measurements were performed after saturating the matrix under high hydraulic gradients. Waste forms would most likely not be exposed to such gradients under field conditions and might therefore have much lower permeabilities. Under such field conditions, convection leaching will be relatively small, and it is important to consider matrix properties related to diffusive leaching, such as connected porosity and matrix tortuosity [*17*].

Durability, either biological, chemical, or physical, refers to the ability of a waste form to keep its integrity after it has been landfilled. Waste forms should be nonbiodegradable as they are essentially composed of inorganic constituents. Chemical durability refers to the interaction of the waste matrix with a leachant. The matrix can be mainly composed of nonhazardous constituents; but if these constituents are soluble in the leachant, a much larger amount of the hazardous constituents will be rapidly exposed. The matrix of cement-based waste forms is insoluble in most ground water environments, as illustrated by the durability of old pozzolan or cement-based structures. The resistance of waste forms to weathering, either freezing/thawing or wetting/drying cycles is, however, low. Data gathered for different types of solidified wastes indicate that samples tested using ASTM Methods for Wetting-and-Drying Test of Compacted Soil-Cement Mixture (D 559) and ASTM Methods for Freezing-and-Thawing Test of Compacted Soil-Cement Mixtures (D 560) typically disintegrate after less than 10 cycles [*15,18*].

Chemical Properties

Figure 3 illustrates the distribution of a chemical element into different fractions that are relevant to inferring long-term leachability. The total concentration is identified either with the aqueous phase of the waste (soluble) or with the solid phase (insoluble). The insoluble fraction is in turn classified as available or unavailable for leaching.

Measurement of the total concentration is strictly an analytical exercise of extraction or digestion. The soluble fraction can be measured in an equilibrium leaching test using a low liquid-to-solid ratio and a mild leachant. The insoluble fraction is obtained by difference.

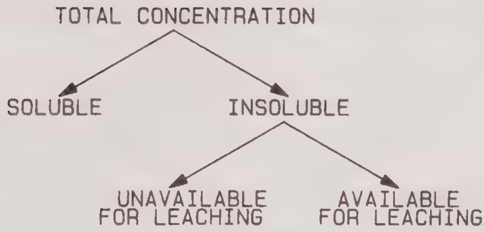

FIG. 3—*Distribution of a chemical element in a waste.*

Further classification of the insoluble fraction as available or unavailable for leaching requires the specification of a chemical environment. The fraction solubilized in low or high pH, oxidizing or reducing environments, for example, can be measured in batch tests where the chemical environment is maintained by punctual adjustment (for example, addition of strong acid to maintain a low pH) or by using a buffered system (for example, acetic acid and sodium acetate). With cement-based waste forms, a sequential chemical extraction procedure has been used to classify the insoluble portion of metals into five fractions [*19*]:

(1) exchangeable metal ions,
(2) surface oxides and carbonate-bound metal ions,
(3) hydroxides and metal ions bound to iron-manganese (Fe-Mn) oxides,
(4) metal ions bound to organic matter and sulfides, and
(5) residual metal ions.

In addition to measuring solubility in a given environment, the waste buffering capacity to resist a change in chemical environment is also meaningful. Cement-based matrices contain chemical compounds (lime, calcium silicate hydrates, and so forth) that have the capacity of neutralizing acid before toxic metals solubilize. This property can be expressed by constructing a titration curve of the waste form and a solubility curve for each of the contaminants that it contains (Fig. 4).

Leaching Model for Cement-Based Waste Forms

The knowledge gained from the measurement of waste form intrinsic properties can be used to develop hypotheses for a leaching model. Hypotheses need to be made about the morphology of the matrix, the transport mechanisms, the composition and hydraulic regime of the leachant, and the method of representing chemical reactions. A simplified version of the model, applicable to leaching of toxic metals under acidic conditions will be presented below. Results and their implications on long-term leachability will not be

FIG. 4—*Titration and solubility curves.*

discussed here. The reader is referred to the original report for a more thorough presentation [*17*].

Morphology of the Matrix

The waste form is represented as a system consisting of several solid phases and a liquid phase. The solid phases include an insoluble skeleton capable of adsorption and a number of chemical precipitates that can dissolve under prevailing leaching conditions. The liquid phase is represented as a network of interconnected pores.

For modelling purposes, the total analytical concentration of a species contained on the waste form must be fractionated as presented in Fig. 3. This is done using the testing methods described in the preceding section. Toxic metals (for example, cadmium, chromium, copper, nickel, lead, and zinc) in cement-based waste forms are normally associated with the insoluble fraction. Under the hypothesis of a mild acidic environment, the total of fractions A, B, and C of the sequential extraction procedure described above are considered available for leaching.

Transport Mechanisms

Based on the low permeability of solidified wastes and on the low hydraulic gradients to which the wastes will be subjected when disposed of by shallow burial, it is assumed that the leachant will not flow through the waste. In absence of convective transport, the only effective transport mechanism is molecular diffusion through the pore-water system of the waste.

In order to simplify the mathematical treatment, it is assumed that the waste form is isotropic and that unidimensional geometry can be used. Taking the aqueous solution/waste form interface as the origin (Fig. 1), a mass

balance for a soluble species i on a slice of the solid leads to the following equation

$$\frac{\partial C_p(i)}{\partial t} = D_e(i) \frac{\partial^2 C_p(i)}{\partial z^2} + \Sigma R(i) \tag{1}$$

where

$C_p(i)$ = concentration of soluble species "i" in the pore solution in terms of mass per unit volume of pore solution, M/L^3,
$D_e(i)$ = effective diffusion coefficient, L^2/T,
$\Sigma R(i)$ = the net effect of all reactions that affect concentration $C_p(i)$ in terms of mass per unit volume of pore solution per unit time, $M/L^3 \cdot T$,
t = time, T, and
z = distance from the interface, L.

$C_p(i)$ is, of course, a function of time t and distance z. The indices have been dropped for simplicity.

Leachant Hydraulic Regime

The waste form specimen is modelled as being completely immersed in an aqueous solution (Fig. 5). The specimen geometrical surface area to leachant volume ratio β is known and constant. The leachant is renewed at a frequency ϕ. These terms can be used to express the leachant velocity v discussed earlier

$$v = \phi/\beta \tag{2}$$

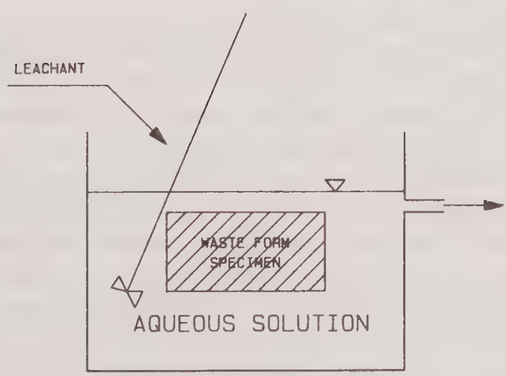

FIG. 5—*Hydraulic regime of the leachant: a completely mixed reactor with the leachant flowing through.*

A mass balance on a species "i" in the aqueous solution leads to

$$\frac{\partial C_i^{(w)}(t)}{\partial t} = \beta\, L_i(t) + \phi\, [C_i^{(l)}(t) - C_i^{(w)}(t)] \tag{3}$$

where

$C_i^{(w)}(t)$ = concentration of species i in the aqueous solution, M/L^3,
$C_i^{(l)}(t)$ = concentration of species i in the leachant, $[M/L^3]$,
$L_i(t)$ = leach rate of species i, $M/L^2 \cdot T$,
β = specimen surface area to aqueous solution volume ratio, 1/L, and
ϕ = leachant renewal frequency, 1/T.

Chemical Reactions

The reaction term of Eq 1 includes all the processes that have the potential of modifying the concentration of a soluble species i, such as precipitation/dissolution, adsorption/desorption, or respeciation. With reference to Fig. 3, these reactions involve species that belong to the fraction "available for leaching." Chemical reactions of protonation or hydrolysis normally happen much faster than molecular diffusion, and an equilibrium approach is retained to describe them.

Numerical Solution

Equations 1 and 3 are coupled since calculation of a leach rate from the solution of Eq 1 is required to solve Eq 3, and the concentration in aqueous solution $C_i^{(w)}(t)$ obtained from the mass balance (Eq 3) is the boundary condition for the solution of Eq 1. These differential equations are also highly nonlinear and are thus solved numerically.

In describing an interacting multicomponent transport system, one set of equations (such as Eq 1 and 3) has to be written for each soluble species. Furthermore, the chemical interactions, at equilibrium in this case, are expressed as stability constants, solubility products, or adsorption isotherms. The result is a set of differential equations coupled to a set of algebraic equations. A solution technique consisting of iterating between the transport and chemical sets of equations is used [*20*]. It involves advancing the numerical solution in time by first solving Eq 1 with the reaction term ignored, and then reestablishing chemical equilibrium at all point in the matrix. This solution was implemented in the model by interfacing a general chemical equilibrium model, MINEQL [*21*], with the numerical solution of the transport equations.

In a simplified version of the model applicable to metal leaching under acidic conditions, it is assumed that H^+ is the only species present in the

leachant and that the chemistry of the system can be described using experimentally determined titration and solubility curves. Figure 6 illustrates how, for the purpose of describing the numerical solution, the matrix can be divided into a series of slices or a series of completely mixed reactors, each containing a mixture of the pore solution and the matrix. The steps involved in advancing the solution in time for the leaching of a metal are described below.

At time $t = 0$, there is a high concentration of H^+ at the interface and a low concentration in the matrix (because of the alkaline environment established by cement). The metal is insoluble, either precipitated or adsorbed, and in equilibrium with a small soluble concentration in the pores. The transport equations are solved to calculate the profile of soluble species in the matrix and advance the solution to time $t = t$. H^+ diffuses in, and some of the soluble metal diffuses out. The model then turns to the titration and solubility curves to reestablish equilibrium (Fig. 4). The cumulative amount of acid that has diffused to each slice (reactor) is used to read the pH on the titration curve and determine the pH profile in the matrix. The equilibrium soluble metal profile can also be determined as a function of pH from the solubility curve. The model then reverts to solving the transport equations based on the profiles corrected for chemical reactions.

The profiles developed in the matrix at a certain time t are presented in Fig. 7, for H^+, the soluble concentration of the metal, and the insoluble concentration of the metal. The inward progression of H^+ has been retarded by its reaction with insoluble form of the metal. A leached layer has developed where the insoluble form of the metal has been depleted. H^+ has not diffused past the leaching front where it is entirely consumed by its reaction with the insoluble form. The soluble metal concentration peaks at the leaching front. There is a gradient for it to diffuse outward, toward the aqueous solution but also inward, further into the matrix. Its progression in the latter direction is,

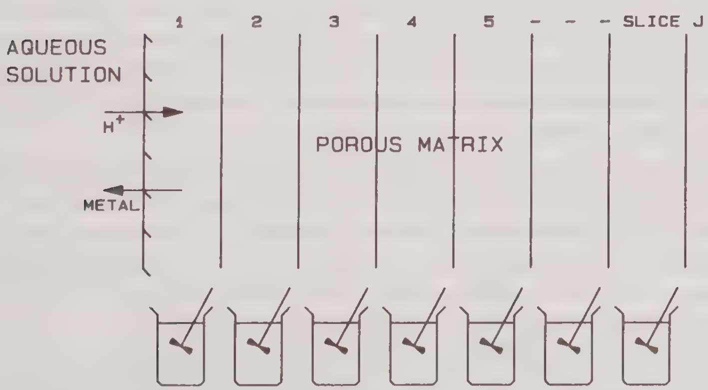

FIG. 6—*Representation of the porous matrix for numerical solution.*

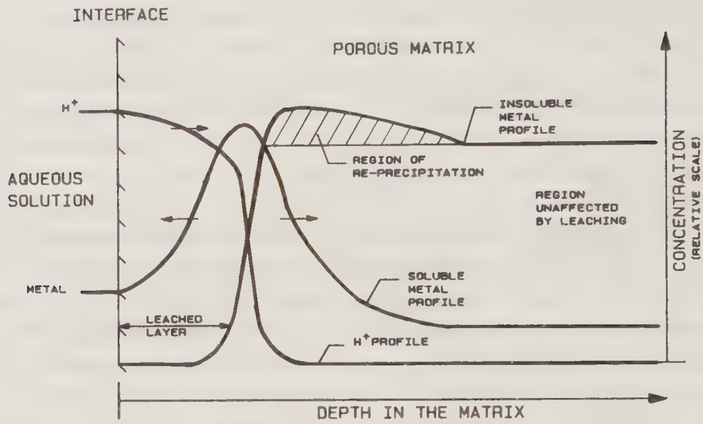

FIG. 7—*Profiles developed in the porous matrix.*

however, slowed down by reaction with excess alkalinity. The metal thus re-precipitates in the matrix, resulting in a concentration of insoluble metal larger than the original concentration (shaded area in Fig. 7).

Conclusion

The leaching of hazardous constituents from waste forms was described from a mechanistic point of view. A general model based on transport mechanisms and on chemical interactions between the waste form and the leachant was presented. It was shown that several mechanisms can control the rate of leaching.

Chemical equilibrium is usually reached or approached in batch laboratory leaching tests. Therefore, their results do not provide kinetic information and can not be interpreted in terms of time. Furthermore, the concentrations measured in the laboratory can be extrapolated to represent field concentrations only for certain ground water hydraulic conditions (for example, static or slow moving ground water).

An approach was presented in which long-term leachability can be inferred based on the measurement of the waste intrinsic properties. Physical properties determine the amount and the way in which leaching water will be contacted with the waste while chemical properties are measured to segregate a contaminant into its mobile and immobile fractions and to determine its availability for leaching in various chemical environments.

A simple mathematical model was developed based on the properties of waste forms containing toxic metals. It can be used to describe the kinetics of contaminant leaching under various leachant characteristics and hydraulic

regimes. Such a mechanistic model, after validation using the results of dynamic leaching tests, can be used to infer long-term leachability.

This approach is proposed as an alternative to using a batch leaching test that attempts to simulate "worst case conditions" for regulatory purposes in the control of hazardous wastes. In designing a leaching test or in interpreting its results, assumptions have to be made about the field leaching conditions. By doing so, one automatically makes sure that the test will not be applicable to a large number of situations. On the other hand, by measuring the intrinsic waste properties related to leachability, one selects a rational, sound base for regulation as these properties can then be used to infer the waste leachability under various field disposal conditions.

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Use of an Upflow Column Leaching Test to Study the Release Patterns of Heavy Metals from Stabilized/Solidified Heavy Metal Sludges

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ABSTRACT: Stabilization/solidification of hazardous liquids and sludges with portland cement has been investigated as a method of treatment that will bind hazardous materials in a form that minimizes adverse effects on the environment after landfilling. Research has been conducted to determine the long-term acceptability of this technique for disposal of heavy metal sludges by determining the rate of release of metals from solidified/stabilized wastes. The primary concern of this research was to determine the manner in which the heavy metals are released from the paste, as this will be important in extrapolation of the short-term leaching test results to long time periods. These studies utilized upflow leaching columns to determine the effects of acid flux (meq/g/day) and waste particle size on the release of metals from the solidified cement paste containing heavy metal sludges. Two particle size ranges and two acid fluxes were evaluated. Leachates from the column were collected on a daily basis and analyzed for pH, alkalinity, cadmium, chromium, and lead. Release patterns were modelled successfully using a diffusion-based equation. An effective diffusion coefficient and leachability index were calculated for each combination of heavy metal, particle size, and acid flux. These values can be used to predict metal release rates.

KEY WORDS: hazardous wastes, leaching, leaching tests, solidification/stabilization, upflow columns, heavy metals, alkalinity, EP toxicity

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Because of increased concern for subsurface environmental quality, many methods of containing hazardous industrial wastes have been investigated. One method for immobilizing inorganic wastes, including heavy metals, is the process of stabilization/solidification.

The stabilization/solidification of heavy metal sludges with portland cement produces a material that is very alkaline. This high alkalinity is beneficial in that it generally renders the heavy metals insoluble but poses a problem from the regulatory standpoint in that standard leaching tests are not aggressive enough to neutralize this alkalinity so as to be able to determine their long-term leachability. For example, the Environmental Protection Agency's (EPA's) extraction procedure only allows the addition of 2 meq of acetic acid to each gram of waste material [*1*]. This has little or no effect on the pH of the leaching environment because of the high buffer capacity of the waste, so that leaching takes place at a pH of 10.0 or higher.

Previous work at the University of New Hampshire has shown that because of the high alkalinity of the solid, 2-meq acid/g leaches little if any detectable metals from a heavy metal sludge solidified with Type II portland cement [*2,3*]. The extraction procedure (EP) test, therefore, is not suited to determination of the behavior of this solid over long time periods when its alkalinity may become neutralized.

The work undertaken in this research was directed toward obtaining a better understanding of the way metals are bound into the solid so that reasonable estimates of long term stability may be made.

For some impervious wastes, the amount of surface area exposed to the leachate will have a direct effect on the amount of water soluble wastes leached from the solid, with the solution of contaminants being directly proportional to the surface area available for leaching [*4–6*]. Therefore, particle size may be an important variable in a leaching test. Previous research at the University of New Hampshire has investigated the differences in amounts of metals leached from a stabilized/solidified waste as a function of particle size [*2,7,8*]. These researchers found that although the smaller particles have more surface area exposed, they leached less metals than the larger particles. They attributed this to increased adsorption and ion exchange capacity of the smaller particles.

In this research, the importance of measuring alkalinity in the leachates is demonstrated as it provides valuable information about what processes are occurring within the column. Studying two particle size ranges simultaneously also allows us to draw some conclusions about how the metals are actually bound into the solid.

Methods and Materials

Synthetic hazardous waste sludges were prepared in the laboratory, stabilized/solidified with Type II portland cement, ground to specific sizes, and the ground particles subjected to an upflow column leaching test.

The sludges were formulated to contain 0.04 mol/L each of cadmium, chromium, and lead. Metals were added as chromium chloride, cadmium nitrate, and lead nitrate and converted to their hydroxide forms in the sludge by neutralization of the solution to pH 8.4 with sodium hydroxide. The sludge was mixed (30 s at 140 rpm, then 60 s at 285 rpm) with Type II portland cement to form a cement paste with a water/cement (W/C) ratio of 1.0 based on weight using ASTM Method for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency (C 305). The sludge was analyzed for total solids by oven drying at 105°C for 24 h followed by weighing. The solids content was used to correct the W/C ratio when the sludges were mixed with cement. The freshly mixed pastes were poured into 3.8 cm diameter by 7.6 cm tall polyvinyl chloride (PVC) cylinders and allowed to set for 24 to 48 h at 100% humidity before they were removed from their molds and returned to the 100% humidity environment. The samples were cured for a minimum of 28 days at a temperature of 22°C.

Cylinders to be used in the extraction tests were broken and pulverized with a mortar and pestle. The particles were mechanically sieved, and the following particle sizes were collected for testing: passing 9.5-mm (3/8-in.) sieve but retained on (9.51- to 4.76-mm) (No. 4) mesh sieve and passing 600-μm (No. 30) but retained on 300-μm (No. 50) mesh.

Column leach tests were performed in the upflow mode. The columns used were Buchner type funnels modified by a glassblower. These columns were 46 mm in diameter by 57 mm high, with a 82-mm neck. The modifications included the addition of a side arm for effluent flow and tapering the neck of the funnel to a pipet-like tip to accommodate narrow bore tubing. A peristaltic pump was used to deliver the leachant to the bottom of the column, through the column neck. Column leachate flowed out of the side arm, located above the waste particles, and into a 500-mL collection flask.

Acetic acid, 0.01 N, was used as the leachant at a flow rate of 0.2 mL/min to create an acid flux of 2.0-meq/g solids/day. The void fraction in the small particle columns averaged 0.58, while in the large particle columns it averaged 0.40. Therefore, the void volume rate of the leachant was 0.13 cm/s for the small particle columns and 0.18 cm/s for the large particle columns. Leachate was collected every 24 h and pressure filtered through a 0.45-μm filter. The alkalinity of the leachate was measured with a recording titrator, and metals concentrations were determined by atomic absorption spectrophotometry.

Results and Discussion

By studying the differences in results between large and small particle extractions, we have formulated some hypotheses about the importance of surface area and alkalinity and about possible differences in binding mechanisms during formation of the solidified product.

The large and small particles showed different results throughout the ex-

traction. It was observed that the small particles turned from their natural cement gray color to a dark gray and then to an orangish brown and finally to a white color. By observing the boundary between the cement gray and dark gray, the progression of acid attack could be closely monitored. The larger particles also turned an orangish brown color but never turned to the white color of the small particles. The progression of acid attack in columns containing large particles was much faster than in columns with small particles. All the large particles turned to an orangish brown color in the first day of the extraction, while the color change of the small particles was a slower progression up through the column.

It is believed that the difference in available surface area between large and small particles led to these color change differences. The small particles had much more surface area exposed than the large particles and therefore had more alkaline species immediately available to neutralize the acidic leachant. As the extraction progressed, this surface alkalinity was rapidly reduced in the bottom of the column and the particles changed color. The large particles had much less surface alkalinity available and therefore the acid passed through the column without being completely neutralized. Therefore, all particles in the column turned color rapidly. In all cases, the time of breakthrough of the orange front at the surface of the column corresponded to the time when the leachate pH dropped below 6.

The alkalinity of the leachate (alkalinity leached from particles) was measured to determine the amount of acid that had been neutralized as the leachant passed up through the column. The ratio of alkalinity leached from the particles to the amount of acid passed through the column (both in meq/g) gave a simple indication of the amount of neutralization taking place. When the ratio was greater than one, the leachant had been completely neutralized and the pH of the leachate was correspondingly high. Therefore, any metals that may have leached from particles near the bottom of the column would have been reprecipitated or readsorbed further up the column. When the ratio was less than one, the pH of the leachate was low and the leachant was no longer being completely neutralized. In these extractions, the time of color breakthrough corresponded to the time when the ratio fell below one. The appearance of metals in the leachate also corresponded to this point in the extraction. Figure 1 shows a comparison of leachate pH and alkalinity/acid ratio.

The amount of alkalinity leached is also an indication of the internal surface area available for leaching. Previous research [2] has shown that calcium hydroxide $Ca(OH)_2$ provides most of the alkalinity that is leached from the particle. It is probably precipitated in the pores of the cement paste after or during the hydration process. As this $Ca(OH)_2$ is leached, more pore space is opened and more surfaces are exposed to the leachant. Figure 2 shows the amount of alkalinity leached as a function of acid passed through the column. It shows the amount of alkalinity leached since the previous analysis (48 h

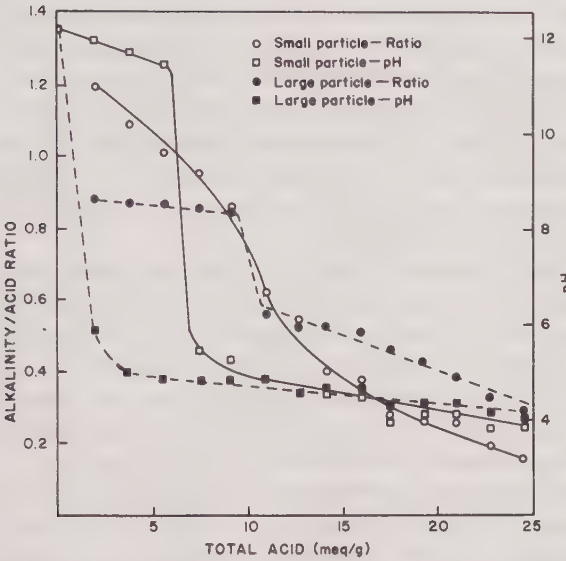

FIG. 1—*Effect of acid addition on the alkalinity leached to acid added ratio and on leachate pH for small (0.3- to 0.6-mm) and large (4.8- to 9.5-mm) size particles.*

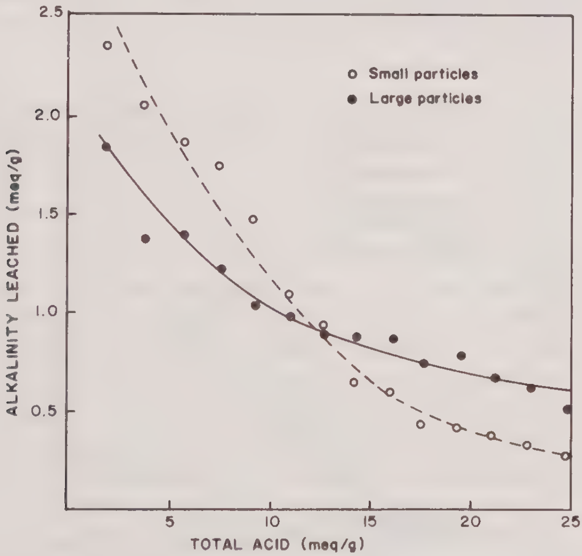

FIG. 2—*Alkalinity leached from small (0.3- to 0.6-mm) and large (4.8- to 9.5-mm) size particles since previous analysis as a function of acid addition (48-h intervals).*

intervals). Notice that the alkalinity leached from the small particles starts out high, providing the buffering capacity that neutralizes the acid in the early portion of the test. It then drops rapidly indicating that surface area available is increasing at a decreasing rate. The large particles leach alkalinity at a slower rate at first, but the leaching rate decreases more slowly than that of the small particles. This indicates that available alkalinity is rapidly depleted in the small particles and that the acid can therefore attack the silica matrix, especially near the bottom of the column. It is believed that this is the point when the particles turned white.

Figure 3 shows the cumulative metal leached as a function of the total acid passed through the column. The metals leached from the small particles started out low, while the acid was being neutralized. It rose rapidly, as might be expected because of the greater surface area available. Cumulative metals leached from the large particles increased at a steady rate. However, the cadmium leached at a much faster rate than the chromium and lead. This may indicate that the metals are bound into the solid differently.

If the cadmium is bound into the solid in the pores or adsorbed on pore surfaces, it would be released along with the alkalinity. Figure 4 shows the cumulative alkalinity leached as a function of total acid passed through the column for both large and small particles. Notice the similarity in the shape of the cumulative cadmium curves and the cumulative alkalinity curves.

Chromium and lead are believed to be bound into the silica matrix itself. Their concentrations were much greater in the small particle leachates where the alkalinity was completely reduced in the bottom of the column and the

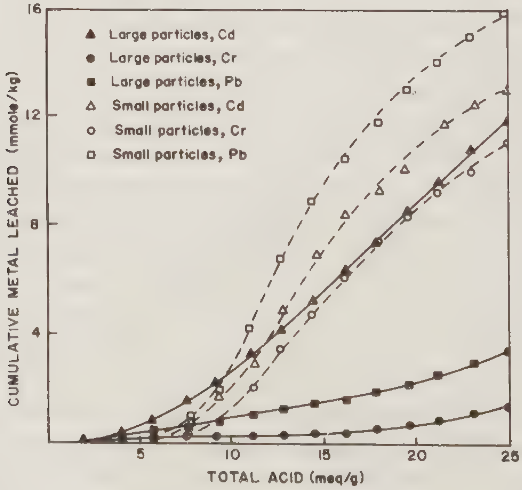

FIG. 3—*Cumulative metals leached from small (0.3- to 0.6-mm) and large (4.8- to 9.5-mm) size particles as a function of acid addition.*

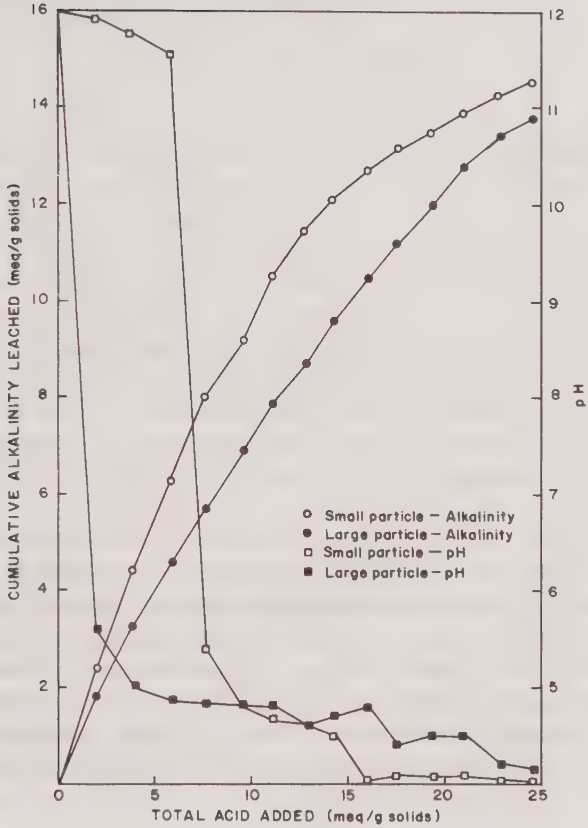

FIG. 4—*Cumulative alkalinity leached from small (0.3- to 0.6-mm) and large (4.8- to 9.5-mm) size particles as a function of acid addition.*

silica matrix broke down. To confirm this, representative samples were analyzed for silicon. It was shown that small particles leached three times as much silicon as the large particles after the initial alkalinity was reduced.

Figure 5 shows a pC-pH diagram for hydroxides of lead, cadmium, and chromium. This diagram was constructed using stability constants from Morel [*9*]. Higher pC values mean less metal in the soluble phase since pC is the negative logarithm of the equilibrium solution concentration. The high pH of the paste as it is being mixed (pH 12 to 13) causes lead and chromium to form soluble hydroxide complexes. Availability of these anions in solution allows them to participate in the formation reactions, possibly much like aluminum. The solid cadmium hydroxide is not available to take part in solution reactions and is trapped in the pores as the solid is formed. This could explain why leachability of chromium and lead appears to be dependent on the disso-

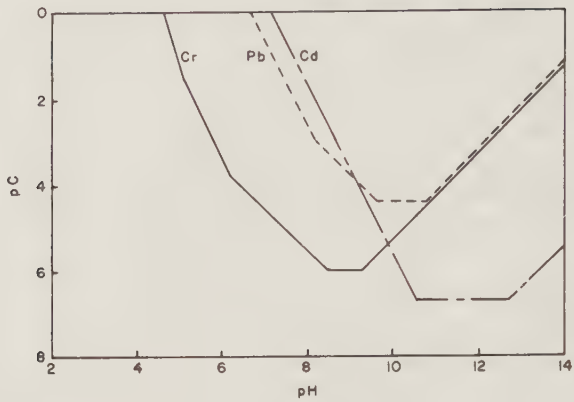

FIG. 5—*pC-pH diagram for hydroxides of lead, cadmium, and chromium.*

lution of the silicate matrix while cadmium seems to be released as alkalinity is leached from the pores. Although the curve shows that only about 10% of the chromium and lead originally present would form the anionic hydroxide complex, more could be formed as that originally present is depleted by solid formation reactions. This hypothesis cannot rule out the possibility of an encapsulation type reaction where lead and chromium hydroxide are surrounded by the silicate fibrils that are formed. However, there is no apparent reason why encapsulation would occur for chromium and lead, and not for cadmium.

Previous researchers have determined that, under mild leaching conditions, diffusion within the solid matrix usually controls the transfer of contaminants from the solid to the surrounding liquid phase [*10, 11*]. A diffusion model that assumes a uniform initial metal concentration in the solid and a zero surface concentration can be expressed as

$$\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right) = 2\left(\frac{D_e}{\pi}\right)^{0.5} t_n^{0.5}$$

where

a_n = contaminant loss during leaching period n, mg,
A_o = initial amount of a contaminant present in the specimen, mg,
V = volume of the specimen, cm^3,
S = surface area of the specimen, cm^2,
t_n = time to the end of leaching period n, s, and
D_e = effective diffusion coefficient, cm^2/s.

The American Nuclear Society (ANS) [*12*] has proposed that the results be

presented as a leachability index LX equal to the negative logarithm of the effective diffusivity

$$LX = \log (1/D_e)$$

This index can be used to compare the relative mobility of different contaminants on a uniform scale that varies from 5 ($D_e = 10^{-5}$ cm^2/s, very mobile) to 15 ($D_e = 10^{-15}$ cm^2/s, immobile) [*9*].

Effective diffusion coefficients and the resulting leachability indices were determined for each metal and each test condition evaluated in this research. Table 1 presents a compilation of LX values. These data again show that cadmium is more mobile in the solidified waste than either chromium or lead. An important finding of this research is that the effective diffusion coefficient for a particular metal is not constant but increases with time as the waste is contacted with increasing amounts of acid. This is probably due to the opening up of pores in the matrix, thus increasing the surface area. This has serious implications for the long-term fate of the material. A metal, such as cadmium, which is relatively immobile in the early years after disposal, may become more mobile over time. It should also be noted that the larger particles have a significantly greater tendency to leach (lower LX values) than the smaller particles, probably because of increased sorption reactions on the surfaces of the smaller particles.

Multiple extraction batch leaching tests were also run for comparison with the column leaching tests [*7,13*]. These consisted of 15 sequential extractions of samples ground to a size that would pass a 9.51-mm sieve and be retained

TABLE 1—*Leachability indices for leaching from large particles (4.8 to 9.5 mm) and small particles (0.3 to 0.6 mm) of stabilized/solidified wastes.*

Extraction Time, Days	Large Particles LX			Small Particles LX		
	Cd	Cr	Pb	Cd	Cr	Pb
1	10.9	14.0	11.2	>15.0	>15.0	13.4
2	10.2	12.3	11.0	13.9	>15.0	13.2
3	9.4	11.7	10.3	13.1	13.1	12.4
4	8.9	11.1	10.0	13.4	13.1	12.0
5	8.7	11.0	9.8	10.6	11.2	10.6
6	8.4	11.0	9.7	10.2	10.4	9.9
7	8.3	10.5	9.7	9.9	10.3	9.8
8	8.3	10.9	9.6	10.0	10.1	9.8
9	8.1	10.2	9.5	10.1	10.2	9.9
10	8.2	10.1	9.4	10.4	10.3	10.1
11	8.0	9.7	9.1	10.5	10.3	10.2
12	8.0	9.5	9.0	10.2	10.3	10.2
13	7.9	9.2	8.7	10.4	10.3	10.2
14	7.9	9.2	8.6	10.5	10.5	10.4

on a 2.00-mm sieve. The particles were placed in 1000-mL pyrex beakers with 500 mL of 0.04 *M* acetic acid. The beakers were covered with parafilm and mixed for 24 h at 20°C on a shaker table with a 2.5-cm stroke at 120 cycles/min. After 24 h of leaching, the liquid was decanted, filtered through a 0.45-μm filter, and analyzed for pH, alkalinity, and metal content. Beakers were then given fresh acid and replaced on the shaker table. This procedure was repeated for the 15 sequential extractions. All experiments were performed in triplicate. A comparison of the leachability indices from multiple batch and column extraction tests for one set of experimental conditions is shown in Table 2. Examination of the data for Days 6 through 14 shows a general trend toward slightly higher *LX* values for the column apparatus than for the multiple extraction procedure, but differences are minimal. On average, the *LX* values for the column tests are about 0.5 units higher than for the batch tests. This means that leaching rates are slightly lower in the column tests, possibly due to incomplete contact between the leachant and the particle surfaces.

These results can be used to predict future leaching rates for the waste material. Table 3 presents predicted cumulative fractions of the initial metal in the waste which would leach over various time intervals, assuming several S/V ratios. An S/V of 0.01 is equivalent to a cube with sides of 6 m each and could be indicative of the original waste block. An S/V of 10.0 represents a cube with 6.0-mm sides, which would be indicative of a material which had lost its structural integrity and crumbled. These data indicate that only very small particles and those with high effective diffusion coefficients will leach

TABLE 2—*Comparison of leachability indices from multiple extraction leaching and column leaching tests.*

Extraction Time, Days	Leachability Index					
	Cadmium		Chromium		Lead	
	Multiple Extraction	Column	Multiple Extraction	Column	Multiple Extraction	Column
1	...	10.9	...	14.0	...	11.2
2	...	10.2	...	12.3	...	11.0
3	...	9.4	...	11.7	...	10.3
4	9.5	8.9	...	11.1	...	10.0
5	8.0	8.7	...	11.0	10.9	9.8
6	7.5	8.4	9.1	11.0	10.0	9.8
7	7.4	8.3	10.8	10.5	9.3	9.7
8	7.5	8.3	10.2	10.9	8.9	9.6
9	7.5	8.1	9.7	10.2	8.6	9.5
10	7.7	8.2	9.4	10.1	8.5	9.4
11	7.9	8.0	9.2	9.7	8.6	9.1
12	8.1	8.0	9.7	9.5	8.5	9.0
13	8.2	7.9	8.9	9.2	8.5	8.7
14	8.3	7.9	8.8	9.2	8.3	8.6

TABLE 3—*Cumulative fraction of metals in stabilized/solidified wastes that will leach over time as a function of leachability index and particle surface-to-volume ratio.*

Leaching Time, Years	Cumulative Fraction Leached					
	$LX = 7$	$LX = 8$	$LX = 9$	$LX = 10$	$LX = 11$	$LX = 12$
			$S/V = 0.01$			
1	0.020	0.006	0.002	0.001	<0.001	<0.001
10	0.063	0.020	0.006	0.002	<0.001	<0.001
50	0.141	0.045	0.014	0.004	0.001	<0.001
100	0.200	0.063	0.020	0.006	0.002	<0.001
200	0.283	0.089	0.028	0.009	0.003	<0.001
500	0.447	0.141	0.045	0.014	0.004	0.001
			$S/V = 0.1$			
1	0.200	0.063	0.020	0.006	0.002	<0.001
10	0.632	0.199	0.063	0.020	0.006	<0.001
50	1.000	0.445	0.141	0.045	0.014	0.004
100	1.000	0.630	0.200	0.063	0.020	0.006
200	1.000	0.891	0.283	0.089	0.028	0.009
500	1.000	1.000	0.447	0.141	0.045	0.014
			$S/V = 1.0$			
1	1.000	0.063	0.200	0.063	0.020	0.006
10	1.000	1.000	0.633	0.199	0.063	0.020
50	1.000	1.000	1.000	0.446	0.141	0.045
100	1.000	1.000	1.000	0.630	0.200	0.063
200	1.000	1.000	1.000	0.891	0.283	0.089
500	1.000	1.000	1.000	1.000	0.447	0.141
			$S/V = 10.0$			
1	1.000	1.000	1.000	0.630	0.200	0.063
10	1.000	1.000	1.000	1.000	0.632	0.199
50	1.000	1.000	1.000	1.000	1.000	0.445
100	1.000	1.000	1.000	1.000	1.000	0.630
200	1.000	1.000	1.000	1.000	1.000	0.891
500	1.000	1.000	1.000	1.000	1.000	1.000

appreciably over time spans up to hundreds of years. The metals evaluated had higher diffusion coefficients and should leach minimally from the stabilized wastes.

Summary

This research demonstrates the importance of testing more than one particle size as it can lead to a greater understanding of the chemistry of the solid. These results also pose a significant problem to regulatory agencies trying to determine what a reasonable particle size to use in toxicity tests should be. If the solid block, which may be 5 m or more in size, fractures into very small

particles, the amount of toxic constituents released to the environment could be significantly different than those released from larger particles or blocks. As shown in this research, the difference in particle size is more important in determining availability of alkalinity than the availability of surface area. In the short term, the large amounts of alkalinity in the small particles is protective, preventing any metals from being released. Once the alkalinity is neutralized, however, the small particles release metals at a much higher rate than the larger particles that are still somewhat protected by the alkalinity inside the particle.

Acknowledgments

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Ground Water and Contaminant Migration Assessments

Robert M. Quigley[1] *and R. Kerry Rowe*[1]

Leachate Migration Through Clay Below a Domestic Waste Landfill, Sarnia, Ontario, Canada: Chemical Interpretation and Modelling Philosophies

REFERENCE: Quigley, R. M. and Rowe, R. K., **"Leachate Migration Through Clay Below a Domestic Waste Landfill, Sarnia, Ontario, Canada: Chemical Interpretation and Modelling Philosophies,"** *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 93-103.

ABSTRACT: The results of field and laboratory investigations of a domestic waste landfill overlying 30 m of natural clay are presented. Four study phases extending over a ten-year period will be summarized.

Concentration profiles for several soluble constituents (sodium, potassium, calcium, magnesium, $C\ell^-$ and dissolved organic carbon) show migration to a maximum depth of ~1.5 m in 15 years. This compares to an advective or seepage advance estimated to be only 3 to 5 cm, indicating migration primarily by diffusion. Concentration profiles for the heavy metals (iron, lead, zinc, and copper) indicate rapid field attenuation with migration to only 10 cm in the carbonate-rich clayey soil.

Graphed solutions to the coupled advection/diffusion equation using constant values for C_0, D, and V_s are only partially successful in predicting the observed chemical profiles because of apparent chemical partitioning at the waste/clay interface. A better fit is obtained by employing an artificial "effective" interface about 25 cm above the observed interface; however, this does not resolve the interface problems.

Recently, new analytical and numerical procedures have been developed for modelling this and other contaminant migration problems. These techniques automatically take into account time-dependent concentration variations within the landfill (for example, because of mass transport into the soil) and allow for a sharp drop in concentration because of surface effects (such as surface smear, drying, and interface partitioning). The numerical solution allows consideration of the effects of a thin but finite interface layer with properties different from those of the underlying soil. Both of these techniques are used in the field case resulting in much superior predictions than earlier models.

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Comments are presented on the significance of this work relative to chemical fluxes through thin clay liners.

KEY WORDS: wastes, diffusion, domestic waste leachate, chemical profiles, modelling, clay barriers

Clay barriers, natural or compacted, are a frequently used method of successfully retarding the migration of chemicals from waste disposal sites. The quantity of chemicals (chemical fluxes) exiting from such liners may be kept very small if advective flow is very slow and chemical diffusion is the main transport mechanism.

The purpose of this paper is to present actual field chemical profiles for a variety of dissolved chemical species migrating primarily by diffusion through thick natural clay deposits below a 15-year old domestic waste landfill and to model these profiles. Typical methods used to estimate the time-rate of migration are discussed. These are followed by a new method to handle waste-clay interface effects (partitioning at the interface) and variable input concentrations (reflecting changes in the leachate). These are followed by examples of chemical flux calculations through thin clay liners to illustrate the significance of correctly modelling the migration profiles.

Site Geology and Soil Conditions

The present soil conditions at the landfill site are illustrated on Fig. 1. Approximately 7.5 m of domestic solid waste, with a 0.5 m clay cover, overlies a homogeneous, massive grey silty clay. The waste projects about 2 m above the surrounding ground surface and was placed in a borrow trench excavated about 5.5 m into the original clay.

The calculated effective stresses shown on Fig. 1 incorporate the effects of a slight downward gradient ($i = \Delta h_t / \Delta L = 0.25$) generated by a small groundwater mound in the waste and drainage into bedrock at ~30 m depth. The variability of this gradient with time and depth is discussed extensively by Goodall and Quigley [*1*]. From extensive laboratory and field measurements of hydraulic conductivity, the average linearized downward pore fluid velocity is believed to be about 0.24 cm/annum [*1*].

The soil in the 3-m zone directly below the waste contains ~34% carbonate, ~25% illite, ~24% chlorite, ~15% quartz and feldspar, and ~2% smectite. About 40 to 45% of the soil is <2 μm in size, and the cation exchange capacity of the <74-μm fraction is ~15 meq/100 g [*2,3*].

The in-situ vertical effective stress plots σ_v' on Fig. 1 show that the clays are overconsolidated by about 90 kPa with a slight increase near the interface. This overconsolidation results in water content values w_n of about 23%, which are mid-way between plastic limits w_p, averaging 11% and liquid limits w_L averaging 32%. In most of our water content profiles there is indication of

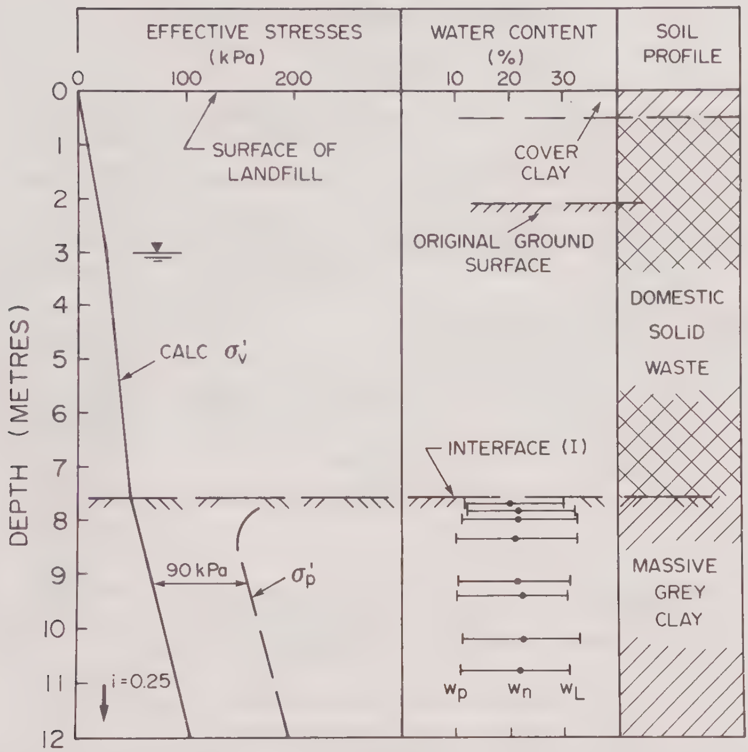

FIG. 1—*Soil conditions at Confederation Road landfill site, 1967 to present* (σ'_v) = *vertical effective stress;* σ'_p = *preconsolidation pressure;* w_p = *plastic limit;* w_n = *natural water content; and* w_L = *liquid limit).*

a water content reduction of 2 or 3% very near the interface as discussed later.

Visually the clay at the interface is a homogeneous grey clay with scattered pebbles and no evidence of staining by the presently overlying black organic sludges. The particulates forming the sludge are generally not identifiable after 15 years and seem to have collected in a firm mat 0.2 to 0.5 m thick. Also, no fissures have ever been encountered in tube samples of the clay even though the base of the landfill probably did not quite penetrate to the bottom of the preconsolidated desiccation crust that exists around the site.

The nature of this crust is further illustrated on Fig. 2 by the preconsolidation versus depth profile drawn from a combination of oedometer measurements and in-situ vane strength results. The upper, 4-m-thick portion of the crust, which has been completely removed at the site, was a stiff to hard, brown oxidized, and fissured clay. The lower portion of the crust was a grey clay about 2.5 m thick with widely spaced brown fissures in the upper 1.5 m.

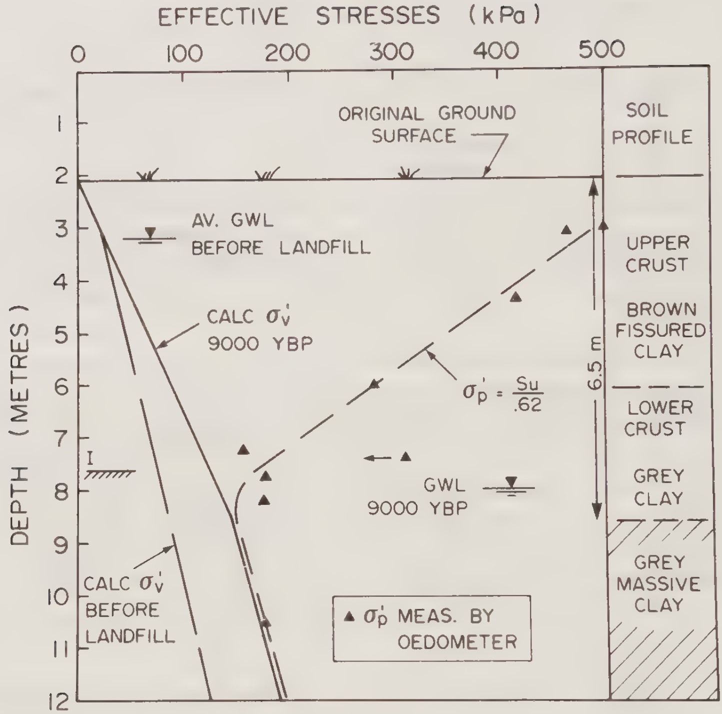

FIG. 2—*Soil conditions 9000 years before present (YBP) and before cutting landfill trench in 1966 (I is waste/clay interface; S_u = undrained shear strength, GWL = ground-water level; see also the legend on Fig. 1).*

All but 1 m of the crust is believed to have been excavated as shown by the figure. A persistent slight decrease in water content of the clays near the interface would in part be due to the effects of the crust.

Chemical Profiles

The range in chemical concentration of Na^+ and $C\ell^-$ in the clay below the waste is presented in Fig. 3 in milligrams per litre of pore fluid. The data indicate overall migration of up to 1.5 m with the erroneous visual impression that $C\ell^-$ is in advance of Na^+. If the same data are plotted in more useful "ground-water" units of mol/m^3, however, the rates of migration of Na^+ and $C\ell^-$ look quite similar (Fig. 4). Since advective transport is believed to have advanced only ~3 cm [*2*], the mechanism of transport must be chemical diffusion from the waste.

The width of the concentration versus depth zones is related to a combination of factors, the most important being scatter in the chemical data associated with sample contamination during tube sampling and a wide variation in

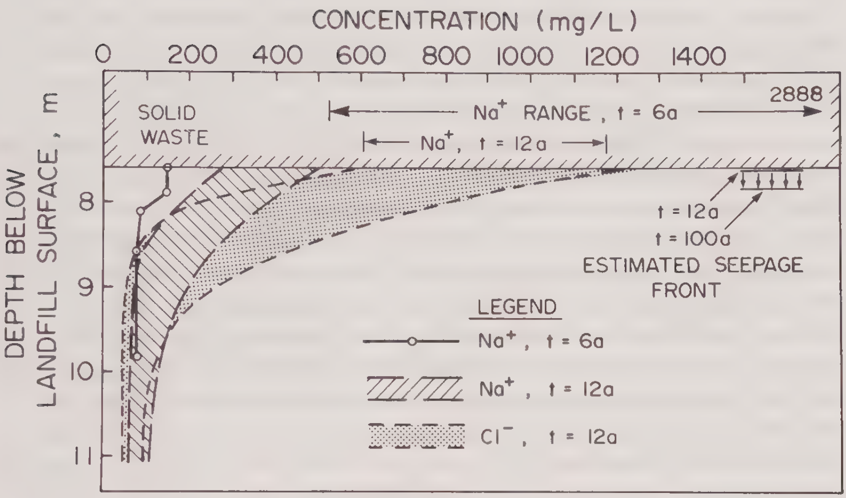

FIG. 3—*Pore fluid concentration of* Na^+ and $C\ell^-$ *(mg/L) in clay below waste after 6 and 12 years of diffusion* (t = 6a *and 12*a) [2].

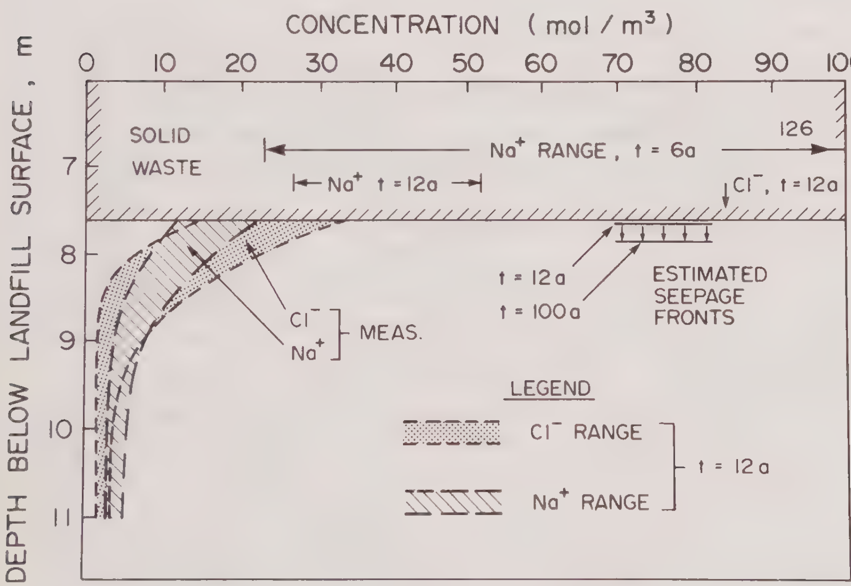

FIG. 4—*Pore fluid concentration of* Na^+ and $C\ell^-$ *(mol/m³) in clay below waste at* t = *12 years* (t = *12*a) [2].

concentration of Na^+ and $C\ell^-$ in the waste from one original dumping spot to another.

Profiles illustrating heavy metal migration are summarized on Fig. 5*a*, which shows total concentrations for copper, lead, zinc, and iron. All of the profiles suggest migration of mobile species to only 10 or 15 cm below the interface, beyond which they stay at background levels. The lead and copper profiles are nearly identical with interface values of ~ 100 μg/g, zinc values at 150 μg/g, and iron values at 40 000 μg/g. Close examination of the interface showed no discoloration in the "metal" migration zone within which *Eh* values of -300 mV indicated strongly reducing conditions. Selective dissolution techniques presently in progress suggest that the migrated metals exist as a complex assemblage of carbonates, hydroxides, and organics.

A final profile for dissolved organic carbon is shown on Fig. 5*b*. In this case migration of the dissolved (<0.45 μm) organic carbon-based compounds appears to have advanced about 1.1 m with maximum values of ~ 40 mol/m^3 near the interface.

Prediction

Early attempts at prediction were carried out without knowing that the clay in the region of the interface was probably less "transmissible" than the clays

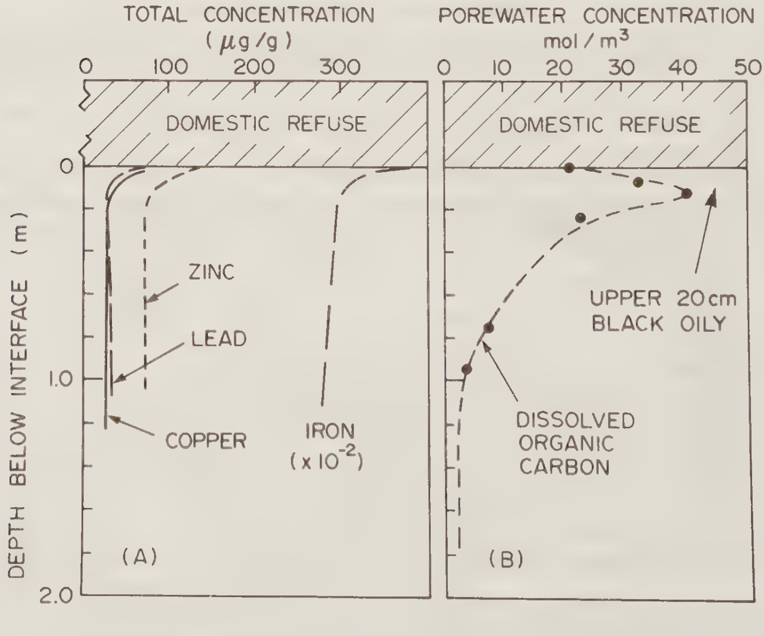

FIG. 5—(a) *Total concentration of heavy metals and* (b) *concentration of dissolved organic carbon* [3].

a metre lower caused by the remaining remnant of the crust and the possibility of partial void plugging by bacteria or precipitated metals. The earliest predictions at $t = 6$ annum [*1*] used an error function technique and ignored the effects of advection. Later predictions [*2*] employed the graphical solution to the one-dimensional contaminant transport equation for coupled diffusion and advection presented by Ogata [*4*]. These predictions assume constant values for influent concentration C_o, diffusion coefficient D, average linearized seepage velocity V_s, and an infinite clay thickness below the waste. Predictions for Na^+ and $C\ell^-$ are plotted on Fig. 6 for $t = 12$ years ($t = 12a$). Input parameters were as shown in Table 1. Although the calculations gave reasonable estimates for the depth of migration, the measured concentrations were well below those predicted in the upper 0.5 m of clay suggesting either very pronounced partitioning at the interface or an "effective interface" above the clay-waste interface observed in the field.

Since the black solid waste sludge seemed to be packed rather firmly against the clay, the next prediction attempt involved shifting the "effective" chemical interface 25 cm above the observed interface and the predictions repeated as shown on Fig. 7 [*3*]. Using $C_o = 86$ mol/m^3, the erratic values

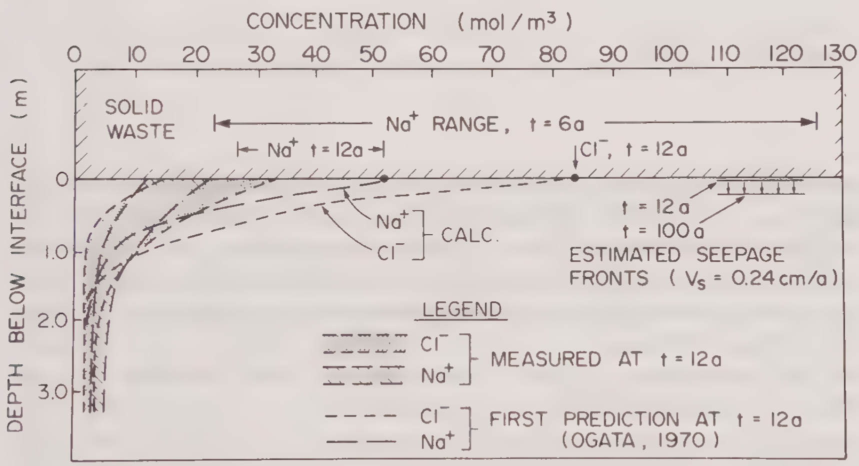

FIG. 6—*Predicted* Na^+ and $C\ell^-$ *profiles using constant values for* C_o, D, *and* V_s [4].

TABLE 1—*Input parameters.*

Na^+	$C\ell^-$
$C_o = 51$ mol/m^3	$C_o = 84$ mol/m^3
$D = 3.5 \times 10^{-6}$ cm^2/s	$D = 6 \times 10^{-6}$ cm^2/s
$V_s = 0.24$ cm/a	$V_s = 0.24$ cm/a

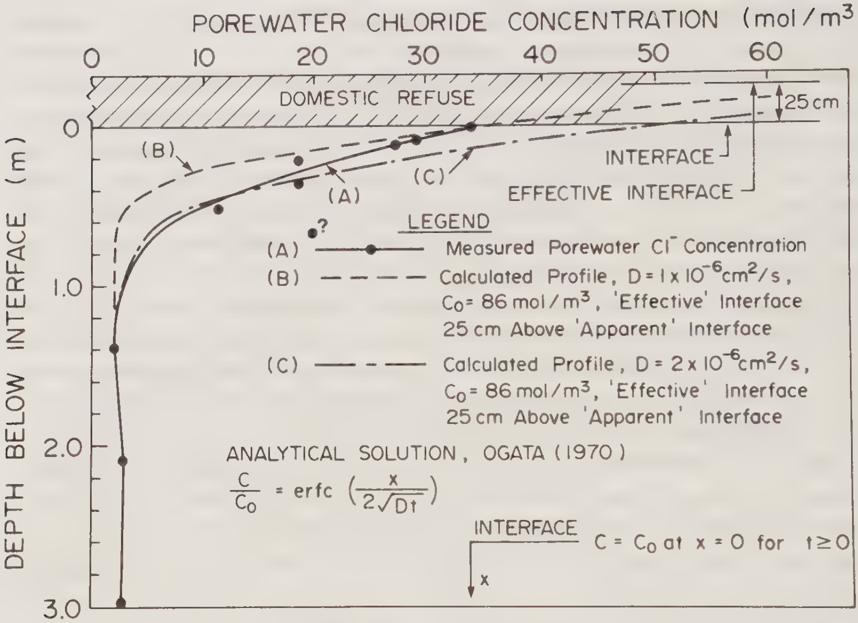

FIG. 7—*Predicted Cl^- profile using "effective" interface 25 cm above observed interface* (*borehole 83-2*, t = *15*a).

plotted for the measured chloride profile (A) could be encased reasonably well by two predicted profiles (B) and (C) using values for $D = 1 \times 10^{-6}$ and 2×10^{-6} cm²/s, respectively. These calculations suggest that the sludge mat could indeed have a thickness within the visually estimated range of 0.2 to 0.5 m. As in all of our work to date, there continued to be considerable scatter in our measured values.

A third prediction approach was carried out using computer program, POLLUTE, proposed by Rowe and Booker [*5*]. This technique permits consideration of a thin interface layer (of thickness H_I) with a diffusion coefficient D_I considerably less than that in the rest of the soil. This technique also allows consideration of the variation of source concentration with time (caused by mass transport into the clay) as well as horizontal flow in an aquifer beneath the clay liner (if present). Calculations were performed varying the ratio D_I/H_I and the dispersion coefficient in the clay to obtain a fit with the data at BH 102 at the Sarnia site after twelve years [*6*]. The best fit was obtained for $D_I/H_I = 0.02$ m/*a* and $D = 0.018$ m²/a (5.7×10^{-6} cm²/s) as shown in Fig. 8. These parameters were then used to predict the concentration profile at BH 101, and the resulting predictions, also shown in Fig. 8, are in very good agreement with the observed concentration profile. The value of

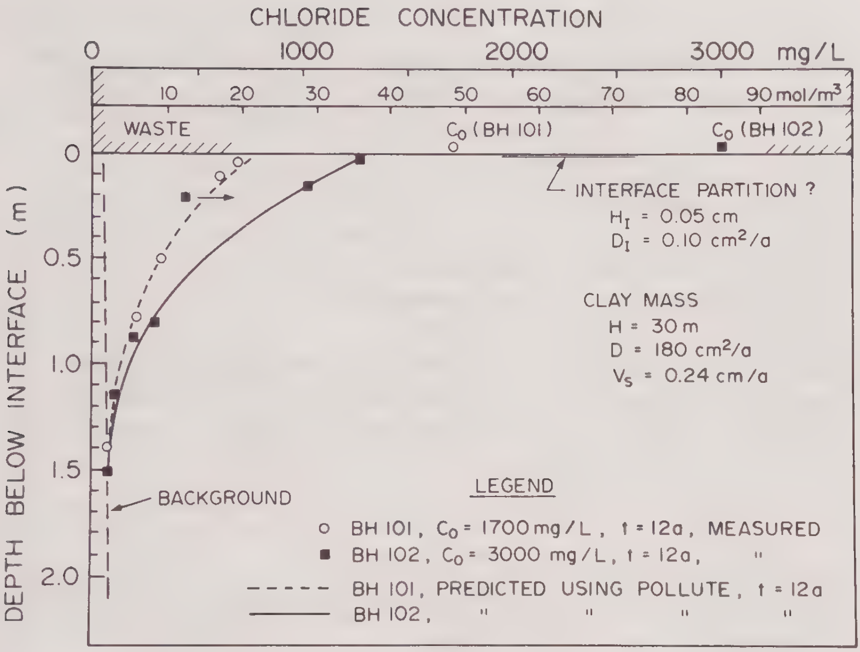

FIG. 8—*Predicted chloride profiles for Boreholes 101 and 102, using POLLUTE* [2,6].

D determined for the main body of the clay is quite consistent with what would be expected in the absence of these data and is, in fact, quite close to the value adopted in the initial attempts to predict the profile shown in Fig. 6.

It is of some interest to note that the precise thickness of the interface layer H_I is not a critical quantity. Essentially, the same concentration profile is obtained for a range of values of H_I provided that the ratio D_I/H_I remains constant (typical values used were $H_I = 0.01$ m and $D_I = 0.0002$ m$^2/a$).

Discussion

It is clear that a reasonable modelling of the concentration profiles at the Sarnia site requires consideration of some form of interface. However, it can also be seen that the backfigured diffusion coefficient of the clay may vary substantially depending upon the assumptions that are made concerning the interface. This may have a substantial effect on the fluxes predicted at any particular time.

Since the chemical diffusion flux F exiting from the base of a liner is directly related to the concentration gradient, $\partial c/\partial x$ at the interface ($F =$

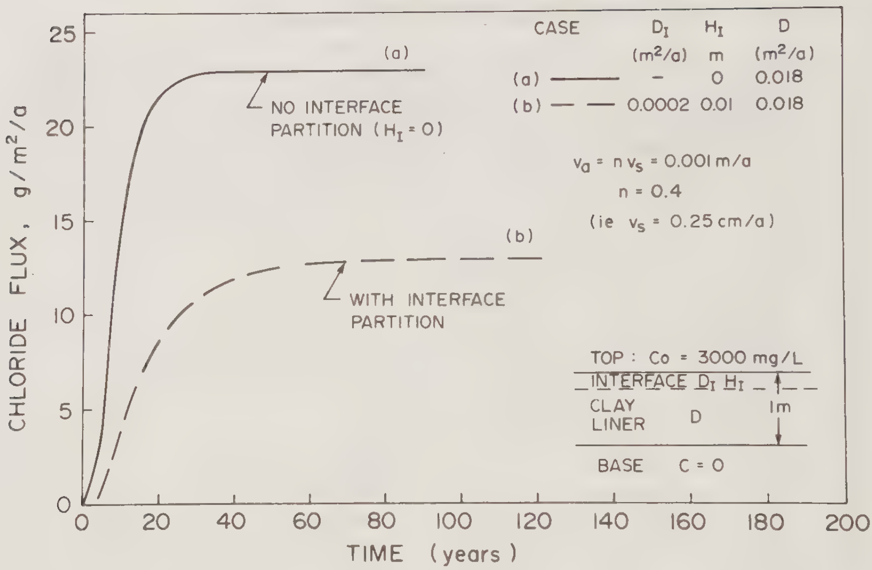

FIG. 9—*Chloride flux-time plots for a 1-m-thick liner:* (a) *no interface partition and* (b) *with interface partition.*

D [$\partial c/\partial x$]), it is important to obtain a correct value. From the previous discussion, predictions of $\partial c/\partial x$ using POLLUTE [7] and a thin interface partition yield lower, more correct values than the simpler Ogata predictions. The significance of this relative to predicted fluxes of chloride through a 1-m-thick clay liner is illustrated on Fig. 9. For these calculations, it was assumed that the influent concentration was constant at C_o = 3000 mg/L, and the base concentration was zero because of a high horizontal flushing velocity in an underlying aquifer. For the case of no interface partitioning, an ultimate chloride flux of 23 g/m^2/a is calculated. For the possible case of a thin interface, an ultimate chloride flux of 13 g/m^2/a is calculated. This represents a large difference that could be very significant is satisfying environmental conditions for a proposed landfill facility.

Finally, for purposes of design, it is generally conservative to neglect the presence of an interface when calculating concentration profiles and fluxes. However, the results presented here show that particular care should be exercised when backfiguring parameters from field data for situations where an interface effect may be present. It also appears that considerable attention must still be given to the effect of a mat of organic particulates that may settle or deposit on top of a clay barrier.

Conclusions

Using measured field values of sodium and chloride concentration profiles in clay below a domestic waste landfill site, a series of modelling efforts were made resulting in the following conclusions:

1. A chemical partition may occur at the waste-clay interface at some sites resulting in an abrupt drop in concentration in the upper 10 mm of clay compared to values in the waste leachate.
2. A new program, POLLUTE, may be used to model both the interface effects and any reduction in leachate concentration caused by migration into the barrier clays.
3. A proper chemical profile (concentration gradient) is required for calculation of chemical flux through clay barriers. In the absence of field data, computer program, POLLUTE, may be very useful for predicting these gradients.

Acknowledgments

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Low-Cost Data Management for Protection of Ground-Water Resources: The Importance of Quality Assurance

REFERENCE: De Ville, W. B. and Malloy, J. A., **"Low-Cost Data Management for Protection of Ground-Water Resources: The Importance of Quality Assurance,"** *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 104–119.

ABSTRACT: U.S. environmental regulations require the collection, statistical evaluation, and reporting of data associated with ground-water monitoring at hazardous waste facilities. Desktop personal computers are capable of managing the large volume of data and automatically generating the required reports. A functional data base for ground-water monitoring data has been developed for the Apple II personal computer. Design emphasis was placed on error-checking during data entry and on simplicity and consistency of all operations available to the user. This should be considered an integral part of quality assurance/quality control considerations, not only throughout the operations of sampling and chemical and physical measurements, but also throughout all operations involving data entry, storage, manipulation, and reporting.

The programming language used in data base development (a structured BASIC) was chosen to facilitate testing and debugging of program modules. A major design objective was to assure that all operations involved in entry, storage, manipulation, and statistical evaluation of data are well-documented and "bug-free."

KEY WORDS: hazardous wastes, ground-water monitoring, microcomputers, data base, personal computer, quality assurance/quality control

U.S. environmental regulations require ground-water monitoring for hazardous waste facilities that may release contaminants into soil or ground water. The primary purpose of such monitoring is to detect, as early as possible,

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releases of contaminants that may threaten ground-water resources. In order to locate these contaminants, it is necessary to do extensive testing of various parameters, which in significant amounts, could cause degradation of the ground water.

A relational data base management system implemented on a desktop microcomputer may be used to assist industries in meeting the state and federal regulations concerning ground-water monitoring. Such a computerized data base can save money and time and be more accurate than a handwritten report that utilizes a calculator for mathematical analyses. Also, this data base can readily be updated, as the information is stored permanently on a disk.

Relational data base management is very significant in the environmental field because of the large number of parameters that must be analyzed from each well. In addition, each test monitoring well must utilize background data from upgradient wells as a basis of comparison to determine whether any statistically significant change has taken place. The combined volume of original data input plus derived computations and statistical decisions may require maintenance of a large data base.

This paper delineates how relational data base management can assist in analyzing the data from ground-water monitoring wells.

Purpose and Scope of Ground-Water Measurement Data

In the United States, regulatory guidance is provided to owners or operators of covered hazardous waste facilities [*1,2*]. Before the installation of ground-water monitoring wells, an evaluation of the site geology and hydrology is required, so that appropriate decisions can be made on the location, screened depth, and other characteristics of the monitoring wells to be installed. Typically, four monitoring wells are required for each hazardous waste facility, such as a land disposal cell, located at a site. One of these wells is to operate as the "background" well and should be a hydrologic upgradient of the monitored facility. The other wells in the facility monitoring group are to be located so as to detect releases of contaminants from the monitored facility.

Following installation of monitor wells, they must be sampled in accordance with a prepared sampling plan. A good overview of sampling procedures can be found in Scalf et al. [*3*].

The actual chemical and physical parameters to be measured following well sampling are a part of the sampling plan, and the list is subject to regulatory review. These parameters may include physical parameters, such as temperature, conductivity, and so forth, as well as chemical parameters such as arsenic, nitrobenzene, and others selected as potential contaminants from the facility.

The measurement methods (physical or chemical) for monitored parameters must also be specific within the sampling plan.

The sampling plan must indicate the quality assurance/quality control (QA/QC) procedures for each step of the sampling episode so that the quality of the data can be ascertained.

Documentation of the QA/QC measures, including the sampling procedures and analytical methods for each data point collected is therefore an integral part of the sampling plan.

Statistical Analysis, Reporting, and Required Actions

The data collected under the sampling/monitoring plan are analyzed to permit a statistical decision as to whether there has been any significant degradation of ground-water quality resulting from leakage of the monitored facility.

An acceptable statistical analysis[3] is Cochran's approximation to the Behrens-Fisher Students' t-test (other statistical demonstrations may be accepted for regulatory purposes).

The results of each sampling episode must be reported together with the results of the required statistical analysis.

An approved monitoring plan under U.S. environmental regulations must contain contingency plans in the event that the statistical analysis indicates significant increases in contaminants in the ground water. In general, the first instance of such a statistical indication of an increase in ground-water contaminants requires notification to the regulatory authority, followed by another sampling episode to recheck the data. If the recheck data also indicate a statistically significant increase in contaminants, then specified actions are required by the regulatory authority. The owner/operator must evaluate for the potential presence of "Appendix VIII" waste constituents, establish a background value for any "Appendix VIII" constituent found, apply for a permit modification to establish a compliance monitoring program, submit information to justify any variation from previous permit requirements, and submit a plan for a corrective action program. Thus, the chemical parameters that must be monitored for may be increased in number for all subsequent ground-water monitoring at the facility.

The Applicability of Computerized Data Management

A computerized data base and reporting system is readily applicable to hazardous waste facility ground-water monitoring and reporting. All important elements of the data management needs of ground-water monitoring can

[3]A discussion of the utility and limitations of statistical tests to determine whether ground-water quality has changed is beyond the scope of this paper. However, it should be noted that in certain circumstances the t-test may be of limited value and could lead to mistaken assumptions about actual trends in ground-water quality.

be specified and can be handled in a systematic, routine fashion, from data entry to reporting the results of statistical analysis of the data.

A computerized data base and reporting system are especially useful in reduction of the routine computations that would otherwise have to be done manually. A well-designed computer system can also reduce the potential of human error in data entry and in computational steps.

Finally, a computerized system can be readily adapted to run alternative statistical tests and to help identify any problems with data validity. For example, it may be highly useful to compare the reported analytical results from different laboratories used to analyze monitor well samples. (It is conceivable that the explanation of a "statistical increase" might be interlaboratory differences, rather than actual leakage of hazardous wastes at a facility.)

Another useful fall-out of computerizing data management and analysis might be to analyze seasonal fluctuations in ground-water gradients. In Louisiana, for example, many hazardous waste management locations are near to the Mississippi River, and ground-water gradients show dramatic seasonal variations because of interaction of river levels with the water table. A computerized system allows relatively simple analyses based upon identification of background well changes that could be correlated to such a situation without the need to reenter monitor well data.

Computerized management of ground-water data is not only cost-effective because of savings in personnel time but can also increase capabilities of data review and analysis.

Considerations for Use of Microcomputers for Ground-Water Monitoring Data

It is often a major, expensive proposition to implement a new data management system on a mainframe computer. This might place ground-water data management on such systems out of reach of small industrial facilities and regulatory agencies on the basis of cost alone.

Desktop personal computers often offer a significant cost advantage, and better availability, by comparison to corporate mainframe systems. They can also offer direct, interactive query and analysis possibilities to the plant or agency personnel interested in a given facility in a way often difficult to achieve otherwise.

Perhaps a major advantage of desktop computers is that with available software tools persons knowledgeable in the objectives of a desired application can actually do the program design and implementation.

But the inherent complexity and size of data bases for ground-water monitoring require careful specification for successful implementation on a desktop computer. Most personal computers have relatively small random access memory (RAM) capacities, limited on-line data storage capacities,

and slow processing speed by comparison to mainframe computers or large minicomputers.

Critical Specifications for Desktop Data Base Implementation

Tricks of the Trade

De Ville has designed a computerized ground-water monitoring data base which is implemented on Apple II computers. The inherent limitation of RAM capacity (64K bytes) was addressed by software reliance on virtual memory (using multi-volume disk storage capacity as the "virtual" size of memory, rather than the limited RAM). The limitations of relatively small disk storage space were addressed by software using (1) data compaction of numerical values to reduce storage requirments, (2) the ability to address multiple volumes of data on disk, so that a data file containing tens of thousands of individual records can be expanded into multiple volumes, yet be addressable as a single file, and (3) using relational data files to minimize the overall size of individual records and so increase storage efficiency.

While the processing speed of Apple II computers is impressive by comparison to manual use of a calculator, the Apple is relatively slow in its native state. Currently available and inexpensive co-processing cards allow a speedup by a factor of 3.6 and give very satisfactory performance in data manipulations by comparison, for example, to the IBM PC.

The ability to carry out data summaries, conditional selections of data, and statistical computations requires that the data base be fully programmable, and especially that the programming be highly modular so that alternate statistical manipulations can be added as required.

The software tools that allow this kind of data base development have not been readily available until quite recently for the Apple II or any other desktop computers in general use. The author's experience with computing dates back to use of a large mainframe computer in the late 1960s and early 1970s. By comparison to the computers of 15 years ago, the current abilities of microcomputers appear almost miraculous, when properly employed.

Recent availability of improved programmable and relational data bases for the IBM PC and compatible personal computers implies the potential of implementation of the ground-water monitoring data system on these computers as well. (However, many software packages have severe limitations on the effective number of records that can be managed or slow operation for the types of application as implemented on the Apple II or both.)

By comment, the author developed a prototype of the computerized ground-water data system using a RAM resident spread sheet. It was quickly apparent that a spread sheet model run on an expanded Apple II, with a model space of more than 500K bytes, would not be sufficiently large to handle many probable cases. Further, the spread sheet model allowed too many

possibilities of human error in data entry and disk manipulations to be satisfactory.

The ground-water data management system was redesigned as a relational data base. This allowed comprehensive program control of routine operations to reduce the potential for operator errors.

Output Specifications

The ground-water data base system was designed to generate printed reports acceptable to a regulatory agency. This is accomplished by a series of modular reports:

- *General Information:* Site name, Environmental Protection Agency (EPA) identification number, facility description, well number, date of well installation, screened depth of well, date of sampling, sample method used, water elevation in well at time of sampling, and so forth. (Most of this information is entered only one time, requiring only new entry of data such as sample date, water elevation when sampled, and verification of a standard sampling method.)
- *Statistical Summary Report:* Sorted by facility name, well number, and physical/chemical parameter. Includes mean concentration, number of replicates, statistical computations (T^* value, t-table values for test and background wells, comparison T, and so forth), decision as to whether an "increase" has occurred, and a flag as to whether or not any replicate exceeded a regulatory standard limit.
- *Data Dump:* Sorted by facility name, well number, physical/chemical parameter monitored; presents actual measurement data, including concentration, concentration unit, detection limit, and analytical method employed for each parameter.

Error Checking and Quality Assurance Considerations

The consequences of poor data integrity are obviously important, especially in management of data that has been gathered under stringently controlled conditions.

The design of a computer data base system should incorporate controlled conditions during data entry and all file manipulations to guard against operator errors. Use of the program should be as simple and consistent as possible, should be well documented, and should allow error-free and comfortable use by clerical personnel during data entry and at report printing time. Although it is impossible to prevent an operator from misreading data to be entered into the data base, and so contributing to error, a great deal can be done to reduce errors. The author's philosophy is that this can be done with-

out excessively intruding on the operator's comfort and the speed of data entry and file manipulations.

Data Entry Safeguards

The most critical opportunities for operator errors occur at the point of data entry. Several general principles have been used:

- On-screen guidance at every step. Prompts are provided as to the available options to reduce operator confusion. Associated with the prompt box is error-checking to ensure that only those commands that are currently available for use will be accepted by the computer.
- Consistency in the program's response to the operator's entries. To the extent possible, a given command should always elicit the same response by the computer.
- Minimizing the data to be entered. General information, for example, the sampling date, should be entered one time only and should be displayed on the entry screen in a "window" together with similar constant information entered during the session. When a change is required for such a "constant" during data entry, the changed data should immediately be verified on-screen.
- Confirming checks on data entered. When the operator enters a well number, the program should first check to assure that this is a legitimate well number. If so, it should confirm the facility number to which that well is assigned. Similarly, when the operator enters a parameter code, for example, "37" for arsenic, the program should first confirm that such a parameter code is valid, then display the name of the parameter, for example, arsenic.
- "Check" Opportunity During Data Entry—The operator should have a chance to confirm or delete a data entry, for example, the arsenic concentration of Replicate 3 before committing the entry.
- Minimum Number of Replicate Data Entries for Statistical Validity—The standard statistical comparison requires a minimum of four sample replicates. The operator should be "flagged" by the program if data entry is terminated with less than four replicates entered.
- Convenient reentry to data entry should be provided if the operator temporarily terminates a long series of entries and then logs on to complete data entry for a sampling episode. The program should display identifying information about the last record previously entered, as well as a running tally of the records entered.

Data Security

Individual program components of the data base are accessed by menu selections, each of which requires verification of a password to proceed. For

example, a clerical can be trained to enter data into the system and provided a password for access to that data base function. However, technical judgment may be called for in assigning background wells against test wells, so that this module can only be accessed when a different password has been verified by the program.

The program also requires assignment of a file code for each site for which data files are created. When individual subfiles are accessed by the program, the operator is asked to enter the correct file code for the site, and this code is verified on the data files before processing can begin. This security step helps prevent inadvertent "mixing up" of data files from different hazardous waste sites.

User Caution Notes

Several of the data base functions permanently modify files. When such a module is summoned by the operator, a caution appears, and the operator is given the option to terminate processing so that files can be "backed up" in the original state before proceeding.

As a final data security measure, access to search and edit modules of the data base are also controlled by unique passwords.

Data Base Description and Computer Terminology

Description of the Data Base Modules

The ground-water monitor well data base system is comprised of a group of data modules, each of which operates within a relational mode with one or more other data modules under program control.

The STANDARD Module

This is a collection of records on disk that already contains code numbers and chemical and physical parameters that may be required to be monitored according to U.S. hazardous waste regulations. When a new data base concerning a particular site is created by the user, the following additional information is prompted for and stored on the STANDARD data disk:

- Site name (company name)
- Site location (for example, city and state)
- Unique code number and description of each hazardous waste facility on the site (for example, 1-southwest landfill)
- Unique number for each monitor well on the site, which is keyed to its location on a particular facility
- Unique file code for all records associated with the site

At the conclusion of each session into which monitor well data are entered into the main ENTRY data module, the STANDARD disk also stores key identifier information on the last record entered on the ENTRY disk, and also the total number of records contained on the ENTRY data disk.

The ENTRY Data Module

This disk (or multi-volume disk series, if many thousands of records have been entered) stores the actual analytical results from a monitor well sampling episode. The records are sorted at time of record entry by facility number, well number, parameter number, sample replicate number, and sample date.

During data entry, the validity of facility numbers, well numbers, and parameter numbers is cross-checked against the set of STANDARD data. Each record contains a set of four replicate results for a parameter. Should the operator enter a data set containing less than the four replicates required by the U.S. regulations, an error message is displayed, and the operator is given the opportunity to complete the data set.

After entry of monitoring data, a program routine may be selected to assign one or more wells as background against each "test" well. Great flexibility is allowed at this stage to account for such factors as seasonal changes in ground-water gradients.

The EPISODE Module

This disk contains records comprising basic information about each monitor well at the site, including date of installation, latitude and longitude, surface elevation, screened depth, date of any maintenance of the well, and so forth. For each sampling episode, the elevation of water in the well is entered.

The STATISTICS Module

This disk contains summary information and the results of statistical comparisons between each monitor well and the well(s) that is assigned as background. The standard statistical routine is Cochran's approximation to the Fisher-Behrens Students' t-test (the statistical analysis program can be readily modified to provide alternative statistical analysis, if desired).

Printed Reports

Several formatted reports are available by menu selection. The report programs provide for user selection of data to be included within a report. For example, results of a sampling episode of a particular date, a range of dates, or all results may be selected.

The GENERAL Report—This report identifies the site (including the U.S. EPA number, company name, location, and (each) facility description). This information is provided as a report for each sampling episode and includes sampling date, elevation of water in each monitor well sampled, sample number for each well, and so forth.

The SUMMARY Report—This report presents a summary of data for each well, including mean concentration of each parameter, a decision as to whether the data set is statistically valid, a decision as to whether or not a significant increase has occurred in the test well by comparison to the background well(s), and a decision as to whether any regulatory limit was violated by either the test well or the background well(s).

The DATA DUMP—This report presents the concentration of each replicate/parameter for each well, the mean concentration, and intermediate and final computations derived from statistical comparisons (including, for example, sample standard deviation, sample variability, *t*-table values, and so forth).

This group of reports satisfies U.S. reporting requirements for ground-water monitoring. In addition, the reporting program modules allow alternative comparisons to be made easily, for example, statistical comparisons between data sets for the same well over selected time series.

A menu-selectable program is being designed to allow automatic graphical presentation of data. The graphics module will automatically calculate and display a regression coefficient for a data time series and also will optionally display the slope of the time series curve.

The Programming Languages

Most of the program commands for operation of the ground-water monitor well data base are executed in BASIC. The numerical precision of nine significant digits is ample for the ground-water data base application; in practice, the precision and accuracy of the actual ground-water parameter measurements do not approach the numerical precision of the BASIC interpreter. This high-level language allows for easy "reading" and modification of programs and also for extensions of the data base routines for additional operations.

Use of S-BASIC for Program Development—Commonly used operations are written as S-BASIC ("structured BASIC") [*4*] modules; a library of such modules can be quickly assembled into different program configurations. An advantage of S-BASIC is that it is a higher level language than Applesoft BASIC, and includes WHILE, LOOP, IF, IF ELSE and ELSE statements not directly available in Applesoft BASIC. Line numbers are not used in S-BASIC statements. BASIC subroutine calls (GOSUB, GOTO, ON. . . GOSUB, ON. . .GOTO) are made to *named* subroutines, rather than to program line numbers.

S-BASIC program modules are written using a text editor or a word processor that produces standard text files. A utility program [*4*] is then used to link S-BASIC modules in any desired order and to convert the linked files into the final runtime program.

Machine Language Routines—All commands affecting disk input/output operations are, however, coded in machine language for maximum speed and efficiency. These machine language routines are available from Stone Edge Technologies, Inc. [*5*] and interface with data file structures designed by the author, using Stoneware, Inc.'s DB Master Version 4+ [*6*] file manager program.

Availability of Illustrative Reports

The author of the ground-water monitoring data base has made no decisions concerning the availability of the data base. However, computer printouts illustrating the performance of the report modules will be furnished to any interested person [*7*]. Those reports resulting from either a violation of a set regulatory limit on a ground-water parameter (for example, pH) or from confirmation of a statistically likely increase in ground-water contaminants show how powerful microcomputer applications can be. They involve conditional choices among a number of alternative reports, which are selected based upon the data encountered in a search of the data base records. For each of the cases cited (violation of a regulatory standard, or statistically likely increase), a draft notification to the regulatory authority is generated as one of the resulting reports. This draft provides detailed information about the incident and provides a "fill in the blanks" approach to documenting the required actions and their schedules, which must be included in the notification to the regulatory authority. The set of alternative documents selected by the computer is accessable by a word processing program for ease of updating and for entry of information, for example, the name and address of the regulatory authority to be notified.

Figure 1 illustrates an S-BASIC routine that requests entry of the current date. The date variable, IN$, is then used to "date stamp" records in the ground-water data base whenever records are added or edited. Figure 2 lists the BASIC code resulting from conversion of the S-BASIC routine. The logical structure of the operation is far easier to follow (and debug) in the S-BASIC version.

Figure 3 presents the main program code for a file merge routine used in development of the ground-water data base. Note the logical clarity of the S-BASIC program. Most of the program's operations are carried out within a LOOP, which repeats data search and processing functions until no more selected records are found by the SEARCH FILE1 subroutine. The last two statements, GOTO CLOSE and END, are "dummy" lines, since the LOOP can only be exited by satisfaction of the IF ZE% > 0 conditional statement following the first statement within the LOOP.

```
*Request today's date.
LOOP
*Loop until correct date entry is confirmed.
  LOOP
*  Loop until a non-blank entry is made.
    HOME
    VTAB 12
    INPUT "Type today's date, YY-MM-DD: ";IN$
    EXIT LOOP IF IN$ <> ""
  ENDLOOP
* Now require confirmation of date entry:
  LOOP
    HOME
    VTAB 12
    PRINT "Today's Date is ";IN$
    VTAB 21
    INPUT "OK (Y/N)? ";A$
    EXIT LOOP IF A$ = "Y" OR A$ = "N"
  ENDLOOP
*Force re-entry unless correct date is confirmed:
EXIT LOOP IF A$ = "Y"
ENDLOOP
*Date has been entered and confirmed.
QUIT
```

FIG. 1—*S-BASIC routine for entry of today's date (note extensive use of comment lines).*

```
10 HOME:
   VTAB 12:
   INPUT "Type today's date, YY-MM-DD: ";IN$:
   IF IN$ <> "" GOTO 60
50 GOTO 10
60 HOME:
   VTAB 12:
   PRINT "Today's date is ";IN$:
   VTAB 21:
   INPUT "OK (Y/N)? ";A$:
   IF A$ = "Y" OR A$ = "N" GOTO 130
120 GOTO 60
130 IF A$ = "Y" GOTO 150
140 GOTO 10
150 END
```

FIG. 2—*Applesoft BASIC converted from Fig. 1 S-BASIC code.*

```
*Merge Parameter Code to SAAGW
*This module comprises the program structure.
GOSUB OPEN
GOSUB MERGE SCRN
ZM = 2
  LOOP
    GOSUB SEARCH FILE1
      IF ZE% > 0
        GOSUB PROMPT CLEAR
        VTAB 21
        PRINT CHR$(7)
        PRINT "NO MORE FILE 1 RECORDS..."
          FOR T = 1 TO 2000
            T = T + 1
          NEXT
        GOTO CLOSE
        END
      ENDIF
    GOSUB SCRN UPDATE
    GOSUB ADD FILE2
      IF ZE% > 0
        GOSUB UPDATE OPTION
      ELSE
        GOSUB FILE2 COUNT
      ENDIF
    ZM = 3
  ENDLOOP
GOTO CLOSE
END
```

FIG. 3—*S-BASIC program used in ground-water data base development.*

Each of the named GOSUB or GOTO subroutines called within the Fig. 3 program is another S-BASIC program module. The final runtime program is prepared by first linking the S-BASIC modules in desired order, then converting the linked system into Applesoft BASIC code.

Summary and Conclusions

It is possible to implement quite sophisticated and demanding data base applications on a desktop computer such as the Apple II series of personal computers. Careful attention to U.S. regulatory requirements during data base development has resulted in a set of software applications that can fully

document and report the required transactions, measurements, and statistical evaluations.

Once preliminary information about the monitoring network at a particular site has been installed within the computer data base, ensuring monitor well data entry and reporting operations can be managed by clerical personnel.

Use of a coprocessor card with the Apple II computer results in satisfactory performance (comparable to or faster than an IBM PC computer) for data entry, editing, and statistical evaluation, even for cases involving a considerable number of monitoring wells.

With some penalties in processing speeds, numerical precision can be expanded well beyond the 9-digit precision of Applesoft BASIC, for example, to 21-digit precision. However, the authors do not believe this is necessary for the ground-water data applications described here.

Consideration is being given to the possibility of compiling the ground-water data applications programs into machine language routines in toto. This is possible in principle, within the 64K RAM constraints of the Apple II computer series, but would require very precise memory mapping for program routine locations and for locations of numeric arrays and string variables. Use of program overlays and of global variables passed between overlay segments is possible and can allow for implementation of quite "large" programs on a microcomputer.

For most real-world situations, however, the set of ground-water data base applications described here is adequate in speed and performance and is much easier to modify for specific circumstances (for example, alternative statistical procedures) that would be a more complex, compiled and overlaid set of program routines.

Computer Terminology

The following includes a brief summary of some of the "computer vocabulary" used.

(1) *Co-processor card:* This is a peripheral card inserted into the computer, which contains a replacement or additional central processing unit (CPU). For example, such cards inserted into an Apple II computer may speed up the computer's processing speed by, for example, a factor of 3.6.

(2) *Data Base:* This is a collection of interrelated data such as the complete collection of information on the ground-water monitoring wells, 'lookup' data tables, data dictionaries, and so forth.

File: A collection of data on a disk that is accessed by a unique name. In this instance, it could be all of the sampling data collected for a particular hazardous waste site.

Record: A group of related fields of information that are treated as a unit. An example would be all of the field data about a particular well.

Field: This identifies a location in a record where a data item is stored, such as by parameters, well numbers, EPA numbers, facility numbers, or date of well installation.

Byte: A unit of information equivalent to one typewritten character, for example, "A" or "3".

(3) *Data Base Management System (DBMS):* This is a package of computer programs and documentation to set up and utilize a data base.

(4) *Data Dictionary:* This is a full description of the fields comprising a record. It also describes each field by name, report heading, length, and data type.

(5) *Entering the Data:* Registering the information within the computer.

(6) *Error Checking:* This computer term limits the number of possible data entry errors by precoding the program to only accept specific information. If the data entry item is incorrect according to prior entry, the operator will be warned by instructions appearing on the display screen.

(7) *Menu:* This is a list of the options that are available for operation within the data base system. This program contains a main menu that presents options for running the major data base operations, for example, data entry, statistical analysis computation, report printing, and so forth. Submenus are defined within specific operation steps to document operations that are available to the operator, for example, record selection for reports.

(8) *Modular Programming:* This occurs when each sector of the source code (instructions to the computer) is set up as a separate section, so that each module may be changed without affecting any other.

(9) *Password Security:* In order to access a certain operation, a password is required. This could also restrict the number of persons allowed to edit or change data.

(10) *Relational Data Base Management System:* This means that the data bases interact with one another. For instance, the sample ground-water monitoring well parameter for arsenic is readily compared with the regulatory limit and a "flag" is raised if it does not conform. In essence, this gives one an electronic "cut and paste" capability to relate different data files to one another.

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Pentachlorophenol Adsorption on Soils and Its Potential for Migration into Ground Water

REFERENCE: Banerji, S. K., Piontek, K., and O'Connor, J. T., "**Pentachlorophenol Adsorption on Soils and Its Potential for Migration into Ground Water,**" *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, C. L. Perket, A. Hamza and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 120–139.

ABSTRACT: The adsorption of pentachlorophenol (PCP) on Missouri soils was studied to determine its potential for migration into ground water. The adsorption data obtained, using low concentrations (0.1 to 10 mg/L) of pentachlorophenol, fit the Freundlich isotherm form. Pentachlorophenol, a weak organic acid, was found to adsorb more completely to Missouri soils as pH decreased, converting PCP to its acid form. High soil organic content was found to strongly increase PCP adsorption. However, most (84%) of the PCP adsorption was reversible. Overall, at the pH values observed (5.7, 6.7), Missouri soils would be expected to retard the movement of pentachlorophenol through adsorption.

KEY WORDS: pentachlorophenol, adsorption, ground water pollution, hazardous materials

Ground water contamination by organic pollutants has become a national problem in the United States [*1*]. The environmental fate of many organic contaminants in ground water is not well documented or understood. The transport of organic contaminants in ground water is affected markedly by sorption and biotransformation processes, which can irreversibly remove the contaminant from solution or simply retard its movement [*2*].

Pentachlorophenol (PCP) is a priority pollutant [*3*], which can cause surface and ground water pollution. Its major usage has been in wood treatment [*4*] and as a herbicide [*5*]. Considering its wide use, it is not surprising that

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PCP has been found in the atmosphere, in rain and snow, in rivers and lakes, in ground waters and in food [*6*]. Understanding the fate of PCP discharge to the environment is particularly important because of its potential hazard to human beings and aquatic life [*7*].

Several investigators have studied PCP adsorption on soils [*8–12*]. Hilton and Yuen [*8*] studied the adsorption of PCP and several substituted urea and triazine herbicides on Hawaiian sugar cane soils. Adsorption of PCP was the greatest of all the compounds studied. The researchers noted that the steep slope of the adsorption isotherm for PCP suggested that large increases in PCP application would be required before a significant increase in the percentage of the chemical in the soil solution was observed. Choi and Aomine [*9*] investigated PCP adsorption on a number of clay soils to determine the effect of humus and clay fractions on the herbicidal effectiveness of PCP applied to soils. All humus-rich soils showed a greatly reduced PCP concentration in the supernatant (soil solution). No relation could be found between the concentration of PCP in the supernatant solution and the soil clay content, the species of the dominant clay minerals, or the cation exchange capacity of the soil. It was found, however, that the concentration of PCP in the supernatant was closely related to the pH of the soil solution.

In a later study, Choi and Aomine [*10*] reported on the adsorption behavior of PCP on several soils having different clay mineral species, organic matter, and pH. The initial concentration of PCP was varied from 12.5 to 500 mg/L. They concluded that the major factor governing the magnitude of "apparent adsorption" was pH. "Apparent adsorption" was defined as the amount of PCP that disappeared from the liquid phase of the soil-PCP system. "Apparent adsorption" occurred to the greatest extent in the strong acid soil system compared to the moderate acid soil system, regardless of the species of clay mineral and the organic matter content. In acid clays, the mechanism of "apparent adsorption" seemed to include adsorption on soil and precipitation in both the soil micelle and in the external liquid phase. Soils rich in organic matter exhibited a greater adsorbance of PCP irrespective of pH. These investigators conducted further experimentation to determine the mechanism of PCP adsorption on soils and also the effects of temperature on such adsorption [*11*]. An adsorption experiment was carried out with allophanic clay separated from soil to evaluate the effect of the amount and particle size of the clay on adsorption of PCP. The equilibrium concentration of PCP in the supernatant solution at pH 5.0 was essentially the same regardless of the amount of clay added. The concentration was in agreement with that expected from the solubility of PCP at pH 5.0, indicating the occurrence of precipitation. Above pH 5.4, the equilibrium concentration of PCP decreased as the amount of clay increased, indicating adsorption of PCP by the clay. Four allophanic soils with pH adjusted to 5.6 by the addition of sodium hydroxide (NaOH) or hydrochloric acid (HCl) were used to measure the adsorption of PCP at 4 and 35°C. Three soils showed a significant increase in PCP adsorp-

tion at the higher temperature, but the fourth soil showed a decrease. The authors explained this difference with the assumption that the andosols (all of which exhibited an increase in adsorption) chiefly adsorbed PCP as an anion, while in the soil showing a decrease in adsorption, the major factor influencing adsorption was van der Waal's force.

In a more recent study, Schellenberg et al. [*12*] reported on the adsorption of chlorinated phenols on natural sediments and aquifer materials. They found that, in the case of PCP, the sorption of the phenolate ion cannot be neglected under ambient pH values. The adsorption was strongly influenced by the organic carbon content of the sorbent and by the ionic strength of the aqueous medium.

It appears that adsorption of pentachlorophenol onto soils has been studied quite extensively. However, in most of these studies, applied PCP concentrations exceeded its solubility limit (greater than 10 mg/L). These studies were generally concerned with the effects of soil adsorption on the biocidal effectiveness of PCP when it is applied as an agricultural herbicide. Other studies were directed at determining the mechanism of PCP adsorption.

The contaminant concentrations that are of concern in ground water pollution descend to the microgram per litre range. Therefore, the adsorptive behavior of PCP at these low concentrations was investigated in this study. The specific objectives of this study were to develop kinetic and isotherm data for adsorption of low concentrations of PCP on two Missouri soils, examine the effects of pH and ionic strength on the adsorption by soils, determine the role of organic matter in adsorption, and finally predict the migration of PCP through soil using the sorption information developed.

Procedure

Soils

Two horizons of a Boone County, Missouri Coppock series soil profile were chosen for study. A surface horizon (classified as AP horizon) and a subsurface horizon (B3t) were selected based on the widely different pH, organic matter content, and cation exchange capacity (CEC) the two soils exhibited. The physical and chemical properties of these soils are given in Table 1.

A humic acid extract was obtained by a method suggested by Blanchar [*13*]. Approximately 1 kg of the surface layer of a soil expected to be rich in soil organic matter was collected from a wooded tract in Columbia, MO. After this soil was shaken in a 5:1 0.5-*N* NaOH/soil solution for 24 h, the supernatant was retained. The pH of the supernatant was lowered to 1.0 by the dropwise addition of concentrated HCl. The precipitate observed at this point was an unpurified humic acid extract. The unpurified humic acid extract was repeatedly washed with 0.5-*N* NaOH to dissolve the humic acid and acidified with HCl to form the precipitate. This washing procedure was repeated until

TABLE 1—*Chemical properties of the Coppock series soils.*

Property	AP Horizon	B3t Horizon
Depth, cm	0 to 18	84 to 120
pHw[a]	6.2	4.8
Cation exchange capacity, meq/100 g	15.5	29.4
exchangeable calcium, meq/100 g	14.48	18.14
exchangeable magnesium, meq/100 g	1.82	6.02
exchangeable potassium, meq/100 g	4.5	3.4
exchangeable sodium, meq/100 g	0.5	3.4
Organic matter, %	15.5	4.6

[a]pHw is the pH of 1:1 mixture by weight of the soil and distilled water.

the supernatant was clear. The precipitate obtained by this procedure was then washed with 0.05-*N* HCl to purify the sample and with deionized water to rinse out excess acid. Approximately 100 g of humic acid extract was obtained in this manner.

Reagents

Purified grade (99+ %) pentachlorophenol was obtained from Research Organics, Inc. of Cleveland, OH. This PCP was used in conjunction with 6.3 mg of carbon-14 labelled pentachlorophenol obtained from Pathfinder Laboratories, Inc. of St. Louis, MO. This radiolabelled PCP was certified as 98+ % pure and has a specific activity of 10.57 mCi/mmol.

The carbon-14 labelled PCP was dissolved in 0.1-*N* NaOH and diluted to a concentration of 7.0 mg/L. Fresh stock solutions of PCP were prepared by adding 1 g of purified grade PCP to 1 L of 0.1-*N* NaOH and mixing until all PCP was in solution.

These solutions were diluted in varying ratios and then mixed to obtain the desired PCP concentration and activity (concentration of labelled compound) for use in the adsorption experiments.

Aquasol-2, a product of New England Nuclear of Boston, MA, was the scintillation cocktail used in this study.

Batch Adsorption Experiments

Batch adsorption experiments were used in determining adsorption kinetics, adsorption isotherms, and adsorption reversibility. These studies were conducted in 150-mL Wheaton glass bottles topped with Teflon®-lined caps. These bottles were thoroughly cleaned with hot water and rinsed with concentrated acid and caustic before every use. The addition of 140-mL PCP solution of known concentration and 14 g of soil to these bottles resulted in mini-

mal remaining airspace in the bottles. This 10:1 solution/soil ratio was employed in most of the batch experiments.

In most of the batch adsorption experiments, ten sample bottles were prepared and used. PCP solutions of seven different initial concentrations, ranging from approximately 0.1 to 10 mg/L, were added to soil in eight bottles (one being a duplicate). To one bottle containing no soil, a PCP solution of known concentration was added to monitor adsorption of PCP by the various containers used in the experimental protocol. One bottle containing soil and a PCP solution lacking any labelled compound was monitored to determine background activity and possible glassware contamination.

These bottles were then placed on a rotary shaker and shaken for the time required for equilibrium (as determined in the kinetic studies). After mixing was completed supernatant samples were obtained by transferring 10 mL of the soil/water solution to a 16-mL centrifuge tube and centrifuging at 15 000 rpm for 5 min in a refrigerated centrifuge. An aliquot of 1-mL of the supernatant was transferred to a 20-mL glass vial containing 10-mL of Aquasol-2 scintillation cocktail. This vial was shaken vigorously and placed in a refrigerator to await counting for determination of the residual concentration of PCP in solution.

The soil/PCP solution mixture remaining in the bottle was then transferred to a 300-mL flask. The soil/water solution was mixed using a magnetic mixer and stirring bar. The pH of the soil/water suspension was determined by immersing a pH probe in the mixture and reading the meter.

The PCP concentration of the supernatant was determined by counting the radioactivity of carbon-14 labelled PCP in a liquid scintillation counter after correcting for quenching and losses during transfer.

Results and Discussions

Kinetic Studies

A kinetic study was done on both soils to determine the time required for equilibrium to be reached. The initial pentachlorophenol concentration used in both cases was 1 mg/L. As illustrated in Fig. 1, nearly 100% of the adsorption that occurred over the course of the 12-day experiment took place within the first 48 h. In subsequent adsorption experiments, a mixing time of 72 h was employed. It was assumed that this extra mixing time would allow for complete adsorption despite any changes in sorption kinetics, which could occur as a result of changing pH, ionic strength, and other parameters.

Adsorption Isotherms

Many studies have reported that the adsorption of organic substances on soil can be described by a linear isotherm [*2*]. The linear adsorption isotherm can be expressed as follows

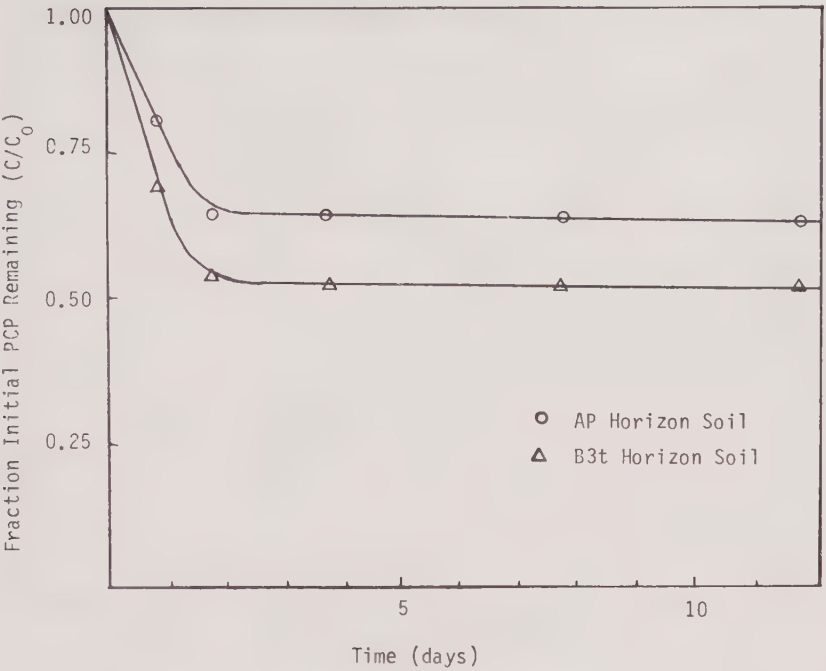

FIG. 1—*Kinetics of PCP adsorption on Missouri soils.*

$$X/M = K_1C \tag{1}$$

where

X/M = number of moles of solute adsorbed per unit weight of adsorbent at equilibrium. Sometimes expressed as micrograms solute adsorbed per gram of adsorbent,

K_1 = constant of proportionality, and

C = solute-phase concentration at equilibrium.

In addition, most contaminant transport models treat adsorption as a linear function because of the difficulties a nonlinear adsorption term creates in solving the governing differential equation [*2*]. However, closer inspection of the adsorption data at low equilibrium concentrations revealed that a linear isotherm was not a very good representation of the isotherm data in this study (Fig. 2).

A Freundlich plot of the same data (Fig. 3) gives more weight to and more accurately describes sorption at low concentrations. Because of this, all sorp-

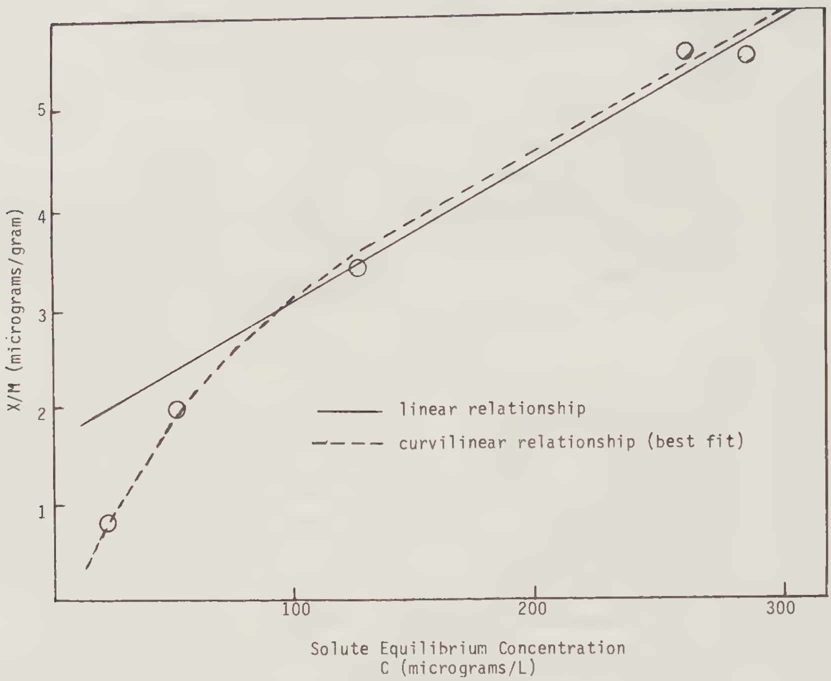

FIG. 2—*PCP adsorption isotherm at low PCP concentrations.*

tion data are presented in the form of a Freundlich isotherm. The Freundlich isotherm takes the following form

$$X/M = K_f(C)^{1/n} \tag{2}$$

where

K_f = Freundlich constant and
n = constant

The initial adsorption experiments conducted in this study were done with "unmodified" soil/PCP solution mixtures, one each for the AP and B3t horizons. By "unmodified" it is meant that the physical and chemical characteristics of the soils were not manipulated with the addition of any other chemicals, and the pH of the soil/PCP solution was allowed to reach an equilibrium value unaltered by the addition of HCl or NaOH.

The Freundlich constants n and K_f for these two batch experiments, along with the constants obtained in all succeeding batch experiments, are presented in Table 2. Because adsorption coefficients are often calculated on an

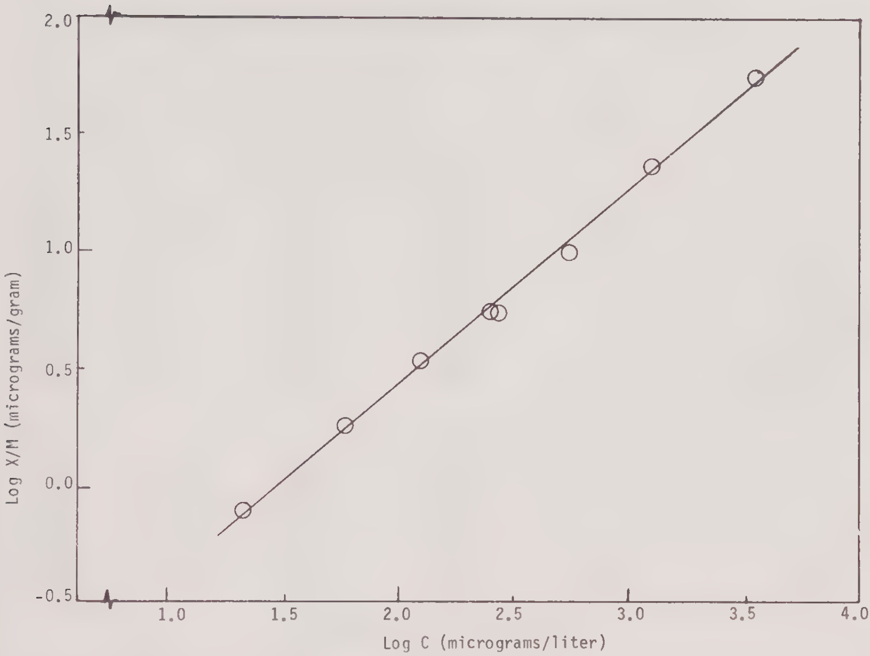

FIG. 3—*Freundlich isotherm of PCP adsorption on B3t horizon soil.*

organic carbon basis K_{oc}, the Freundlich constants in Table 2 are also presented in this manner. The Freundlich equation based on the organic carbon content of the adsorbent is expressed as follows

$$X/M_{oc} = K_{oc}\,(C)^{1/n} \tag{3}$$

where

X/M_{oc} = mass of solute adsorbed per unit weight of organic carbon content of the adsorbent and

K_{oc} = Freundlich constant based on the organic carbon content of the adsorbent.

The K_f constants were converted to the organic carbon basis using the following relationship

$$K_{oc} = K_f/f_{om} \times 1.724 \tag{4}$$

where

f_{om} = the fraction of organic matter in the soil and

1.724 = conversion factor for organic matter to organic carbon [*14*].

TABLE 2—*Summary of adsorption isotherms.*

	Freundlich Constants [2]				
Treatment	pH	n	K_f	K_{oc}	r^{2a}
		AP HORIZON			
. . .	6.8	1.33	0.029	32.2	0.999
HCl	5.8	1.40	0.060	66.7	0.987
HCl	6.1	1.45	0.042	46.7	0.998
NaOH	7.1	1.30	0.016	17.8	1.000
NaOH	7.5	1.22	0.007	7.8	0.996
NaOH	7.9	1.07	0.002	2.2	0.991
NaCl (100 mg/l)	6.5	1.26	0.025	27.8	0.994
NaCl (250 mg/l)	6.6	1.26	0.026	28.9	0.999
NaCl (500 mg/l)	6.7	1.29	0.031	34.4	0.997
		B3T HORIZON			
. . .	5.6	1.26	0.035	117	0.998
HCl	4.2	1.20	0.058	193	0.998
HCl	4.8	1.79	0.154	513	0.995
NaOH	5.7	1.22	0.017	56.7	0.996
NaOH	6.1	1.30	0.012	40.0	0.996
NaOH	6.6	1.25	0.005	16.7	0.993
		HUMIC ACID EXTRACT EXPERIMENTS			
	4.1	1.08	0.219	0.38	1.000
	4.9	1.14	0.054	0.33	1.000

[a] r^2 = coefficient of determination.
[b] 3.95-g purified humic acid extract and 140-mL PCP/water solution.
[c] 3.95-g mixed with 14-g B3t and 140-mL PCP/water solution.

The Freundlich adsorption isotherms for these two batch experiments, presented in Fig. 4, show that the B3t soils adsorbed PCP more completely than the AP soil. This was a bit surprising in light of the fact that the AP soil contained approximately three times as much organic matter as the B3t soil. Increased organic matter content is the soil parameter most often linked to increased adsorption of neutral nonpolar organic compounds by soils. The B3t soil does have a greater CEC than the AP soil, but this would not be expected to greatly influence the adsorption of pentachlorophenol, a weakly acidic organic compound.

The pH of the B3t soil/PCP solution suspension was measured as 5.7, compared to a suspension pH of 6.7 for the AP horizon. The pH of the soil suspension will determine the degree of dissociation of a weak acid like PCP. Whether a compound is present in the molecular or ionized form can affect both the extent and magnitude of adsorption of an organic compound and the strength by which it is held since the energy of adsorption may be vastly different between the dissociated and molecular form [*15*]. The acid dissociation constant of PCP is reported to be 5.25 [*12*]. Therefore, it would be expected

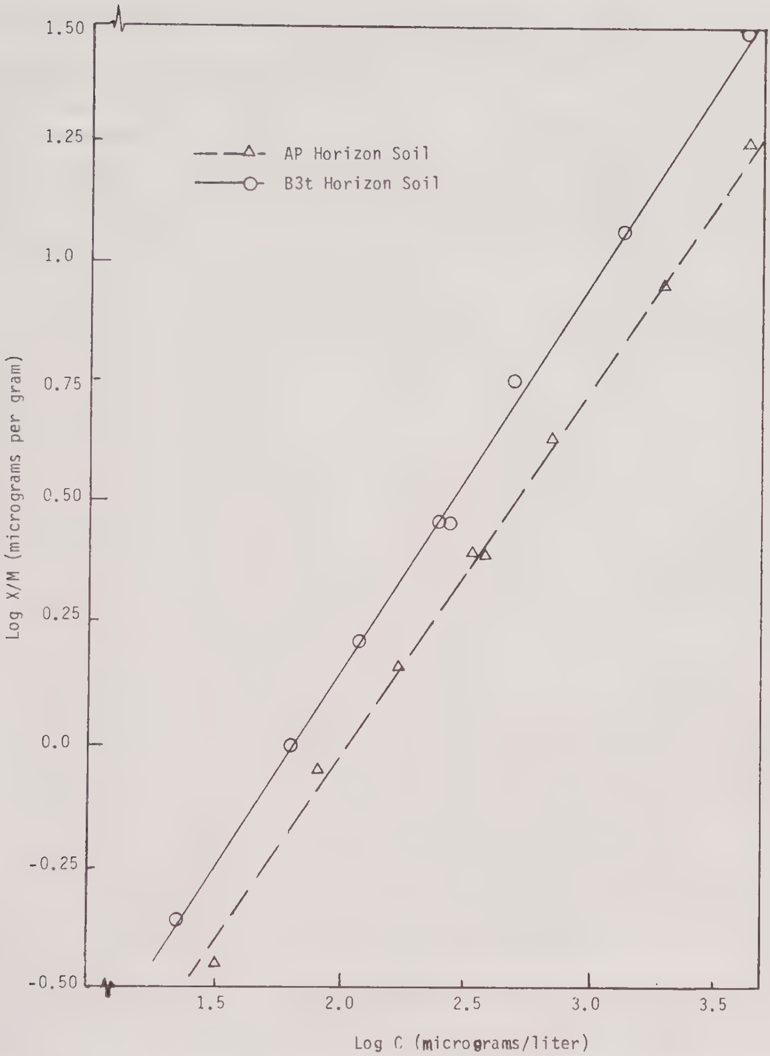

FIG. 4—*Freundlich adsorption isotherms for AP and B3t horizon soils at an "unmodified" pH.*

that the higher pH (6.7) of the AP horizon soil would increase the dissociation of PCP and, therefore, decrease adsorption.

Effect of Soil Suspension pH

An investigation of the effects of soil suspension pH on the adsorption of PCP was then conducted. For both the AP and B3t horizon soils, the suspen-

sion pH was adjusted by the addition of NaOH or HCl. Freundlich adsorption isotherms were obtained by the batch method.

Pentachlorophenol adsorption by both B3t and AP horizon soils clearly increased with decreasing pH, as illustrated in (Fig. 5). The Freundlich isotherms of maximum and minimum adsorption for each soil (corresponding to the lowest and highest adjusted pH values) are presented in this figure. Another description of this trend toward increased adsorption with decreasing pH is presented in Fig. 6. In this figure percentage (%) removal was calcu-

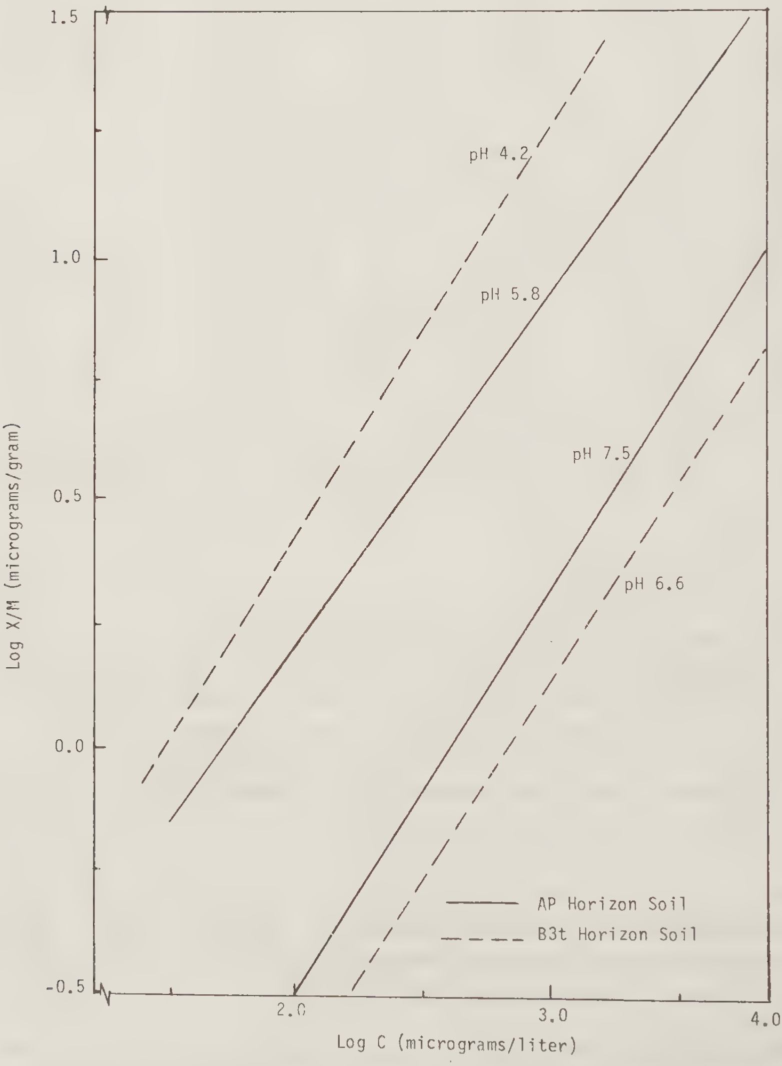

FIG. 5—*Freundlich adsorption isotherms for the pH range used in study.*

lated by determining the amount of PCP that would be adsorbed by 14 g of soil from 140 mL of a 1-mg/L PCP/water solution as predicted by the Freundlich equation. Freundlich constants used in the calculation were obtained from the appropriate isotherm.

Hamaker and Thompson [*16*] reviewed several studies concerning the adsorption of weakly acidic organic compounds by soils and concluded that weak acids are very much more highly adsorbed when in the free acid form as compared to the anion. Anions tend to be repelled from the negatively charged clay surfaces, inhibiting adsorption at these sites. Repulsion of the anion by the predominantly negatively charged surface of organic matter can also reduce adsorption. The dissociation constant of acidic groups in humic acids (carboxyl [COOH]) plus phenolic- and enolic-hydroxide [OH]) is in approximately the same range as that of PCP, 4.5 to 5.5. As this pH range is approached, increased adsorption of PCP by organic matter could be attributed to the hydrogen bonding of molecular PCP with the COOH, carbonyl (C=0), and amide (NH_2) groups of organic matter. Adsorption of pentachlorophenol onto organic matter through hydrophobic bonding would also increase as both the PCP and organic colloids become less polar (acid form).

As can be seen from Fig. 6, for adsorption at the same suspension pH, the surface soil (AP) adsorbed more PCP than the subsurface soil (B3t). This may be due to the higher organic matter content of the surface soil. Figure 7 is a plot of the removal of PCP on an organic carbon basis as a function of pH. In this figure, removal is represented by X/M_{oc}, the amount of PCP adsorbed per unit weight of organic carbon. X/M_{oc} values were computed using the appropriate Freundlich constants and assuming an initial PCP concentration of 1 mg/L. This figure illustrates, that for the same suspension pH, the sorptive capacities of the two soils are quite similar when viewed on an organic carbon basis. The B3t soil, in fact, exhibits a higher PCP adsorption per gram of organic carbon than the AP soil. This contrasts with the difference between soils illustrated in Fig. 6, where adsorption is presented on a "total soil weight" basis.

To further elicit the role of organic matter content in the adsorption of PCP by these soils, additional batch adsorption experiments were conducted.

Influence of Soil Organic Matter

A PCP/water solution (140 mL) was placed in two sets of sample bottles. Approximately 4 g of purified humic acid extract was added to one set of bottles. To another set of bottles a mixture of approximately 18 g of a mixture of approximately 4 g of purified humic acid extract and 14 g of B3t horizon soil were added. The soil/humic acid extract mixture was mixed for a four-day period before use in this experiment. After mixing, steady state pH values were measured and Freundlich isotherms were constructed from the resulting data.

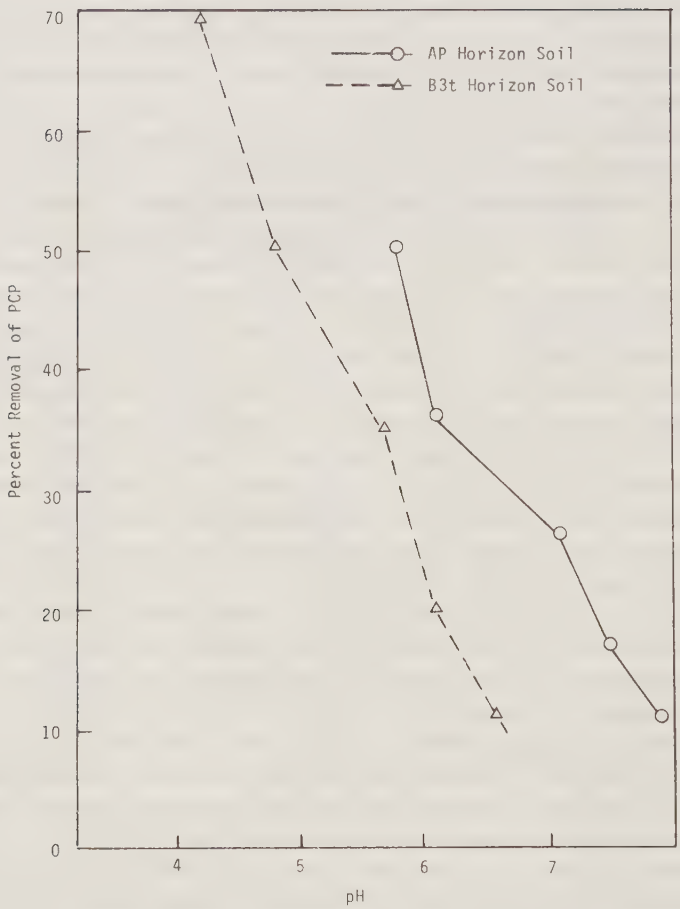

FIG. 6—*The influence of pH on the removal of PCP from solution.*

X/M values were then computed on a total soil and on organic carbon basis. An initial PCP concentration of 1 mg/L was assumed. The results of these computations were presented in Table 3. On a total soil basis, the X/M values of the humic acid extract and the humic acid extract/B3t soil mixture were higher than the X/M values of the B3t soil at a similar pH. This indicates the importance of organic matter in adsorption. When computed on an organic carbon basis, however, the X/M_{oc} values of the humic acid extract and extract/soil mixture were dramatically lower than the corresponding X/M_{oc} values of the B3t soil.

Hamaker and Thompson [*16*] noted that, whereas adsorption coefficient values for soils high in organic matter content are much higher than those of "normal" soils, the values of the adsorption coefficient on an organic carbon basis K_{oc} are usually much lower than the corresponding K_{oc} values of normal

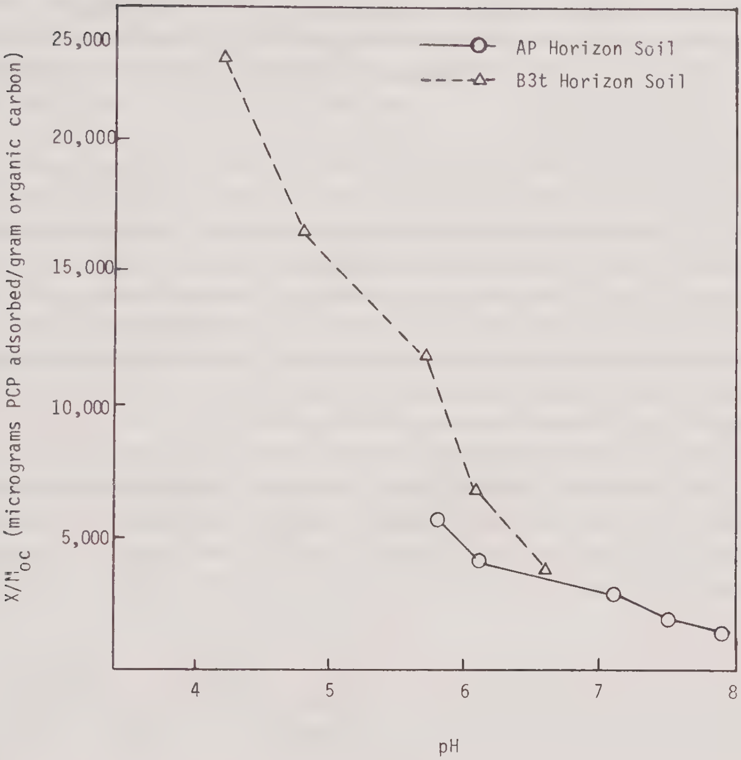

FIG. 7—*The influence of pH on the amount of PCP adsorbed per unit weight of organic matter* X/M$_{oc}$.

TABLE 3—*The effect of increased organic matter on* X/M.

Sorbent	pH	*X/M*	*X/M*$_{oc}$
Humic acid extract	4.1	28.6	49.3
B3t horizon soil	4.2	6.6	22 000
Extract/soil mixture	4.9	7.0	42.2
B3t horizon soil	4.8	4.9	16 300

soils. This may be due to a "piling up" of the organic matter, which limits the adsorbing surface per unit weight of organic matter in soil [*17*].

Effect of Ionic Strength

The effect of ionic strength on the adsorption of PCP by soil was determined by conducting batch adsorption experiments on both soils using PCP/water solutions containing 100, 250, and 500 mg/L sodium chloride (NaCl).

The Freundlich constants for the NaCl treated soils in Table 2 show little variation. This data indicate that in the range of ionic strengths used in this study, ionic strength exerts no significant effect on adsorption of PCP.

Adsorption Reversibility

The reversibility of PCP adsorption by the surface soil was examined by conducting the standard batch adsorption experiment (140 mL of PCP/water solution and 14 g of soil), centrifuging the entire sample bottle to retain the soil, sampling and discarding the supernatant, adding 140 mL of "clean" deionized water, and then mixing for the 72-h equilibration time. Two desorption isotherms were obtained in this manner. A final desorption was done using an organic solvent (2-propanol) instead of water. The results of these desorption experiments are presented in Table 4.

The amount of PCP adsorbed ranged from 0.85 to 15.7 μg/g. The percentage of PCP initially adsorbed that was desorbed during the three washings averaged 84%. The bulk of the total PCP desorbed in the three washings was desorbed in the first washing. The amount of PCP not recovered in the three washings varied from 0.20 to 1.39 μg/g soil. Choi and Aomine [*11*] also found

TABLE 4—*Results of desorption experiment.*

	X/M, μg PCP/g soil					
		Desorbed				
C_e[a]	Adsorbed	#1 (water)	#2 (water)	#3 (2-propanol)	Remaining	% Recovered
6040	15.73	10.87	2.08	2.29	0.49	96.9
6290	13.21	8.14	1.83	1.88	1.36	89.7
3020	9.06	5.14	1.23	1.47	1.22	86.5
3120	8.13	5.01	1.21	1.45	0.46	94.3
1260	4.65	2.38	0.64	0.80	0.83	82.1
1280	4.44	2.37	0.62	0.86	0.60	86.6
700	2.89	1.33	0.38	0.59	0.59	79.6
420	1.95	0.81	0.24	0.45	0.45	77.0
430	1.88	0.86	0.24	0.40	0.39	79.5
165	0.85	0.33	0.10	0.21	0.21	75.0
165	0.85	0.33	0.10	0.22	0.20	76.7
			FREUNDLICH CONSTANTS			
n	1.29	1.02	1.03	1.00	...	...
...						
K	0.017	0.009	0.009	0.007	...	...
K_{oc}	18.9	10.0	10.0	7.8	...	...
r^2[b]	1.00	1.00	1.00	1.00	...	...

[a]Equilibrium PCP concentration in initial adsorption experiment (micrograms per litre).
[b]r^2 = coefficient of determination.

that the adsorption of PCP to soil was reversible. The possible strengthening of the PCP-soil bond with time was not investigated in this experiment.

Breakdown of PCP to carbon dioxide would have been required for the labelled ring carbon atom of PCP to escape detection. The relatively short time involved in the experiment and the absence of an acclimated microbial population makes it unlikely that microbial degradation contributed significantly to the amount of PCP not recovered. Rather, it appears that a fraction of the PCP initially adsorbed was adsorbed irreversibly.

Other investigations of adsorption of organic substances onto soil have confirmed that desorption appears to differ from adsorption in being slower and also in that a portion of the adsorbed material is very difficult to remove. Desorption isotherms reflect the higher retention of the chemical on the solid [*16*].

By examining the Freundlich constants in Table 4, one can see that the adsorption/desorption isotherms are not single valued. This indicates that a contaminant transport model probably cannot exactly describe contaminant retardation (adsorption) using a single adsorption coefficient to describe both adsorption and desorption.

An Evaluation of the Effect of Adsorption on PCP Migration in Ground Water

Given the adsorption coefficients determined in this study, what effects does adsorption of PCP onto soil have on the transport of PCP in ground water?

As discussed earlier, most contaminant transport models treat adsorption as a linear function. Substitution of the expression for linear adsorption into the governing differential equation yields a term commonly called the retardation factor R_f. The retardation factor is given by the equation

$$R_f = V_{gw}/V_c = 1 + (\rho/\Theta)K_1 \tag{5}$$

V_{gw} = the average linear velocity of the ground water,
V_c = the velocity of the $C/C_o = 0.5$ point on the concentration profile of the adsorbing contaminant (see Fig. 8),
ρ = soil bull density,
Θ = porosity, and
K_1 = constant of proportionality in the linear adsorption isotherm (Eq 1).

Freeze and Cherry [*18*] report that the retardation factor R_f for unconsolidated granular deposits is generally in the range given by

$$R_f = 1 + 4(K_1) \text{ to } 1 + 10(K_1) \tag{6}$$

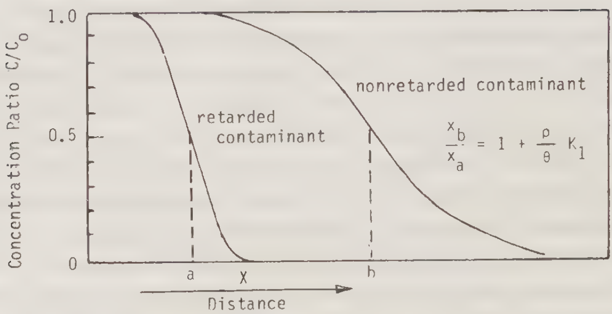

FIG. 8—*Advance of adsorbed and nonadsorbed contaminants through a soil column.*

Equation 5 assumes a value of porosity of 0.2 to 0.4 and a bulk mass density of 1.6 to 2.1 g/cm^3. The required dimensions of K_1 in the expression are millilitre per gram, the units in which K_1 is normally reported.

A number of linear adsorption coefficients and corresponding retardation factors are presented in Table 5. The adsorption coefficients were linearized by computing X/M values from the appropriate Freundlich relationship at the equilibrium concentrations of 75 and 5000 μg/L, the upper and lower concentration limits on which the Freundlich adsorption isotherms were determined. The slope of the line defined by the plot of these X/M values versus their corresponding equilibrium concentrations is the linear adsorption coefficient K_1.

Table 5 contains values of K_1 and R_f for the Ap and B3t horizon soils that were computed based on the "unmodified pH" adsorption isotherms and measured soil properties. The other values of K_1 and R_f listed in Table 5 are hypothetical upper and lower limits on K_1 and R_f values for PCP adsorption at the concentrations used in this study. These values were computed based on the adsorption isotherms of maximum and minimum adsorption (the B3t horizon soil at pH 4.2 and the B3t horizon soil at pH 6.6, respectively) and Eq 6. Calculated retardation factors for the "unmodified" soils (R_f = 12, 23)

TABLE 5—*Linear adsorption coefficients and retardation factors.*

Soil Horizon	Porosity	Bulk Density, g/cm^3	K_1, mL/g	R_f
AP	0.5	1.32	4.0	11.6
B3t	0.4	1.56	5.9	23.4
B3t at pH 4.2	$1 + 10(K_1)$[a]		13.8	139
B3t at pH 6.6	$1 + 4(K_1)$[a]		0.9	4.9

[a]From Eq 5.

indicate a ground water velocity an order of magnitude faster than the $C/C_o = 0.5$ point of the contaminant plume and suggest that PCP is significantly retarded by adsorption to soil during transport by ground water.

The importance of adsorption in retarding contaminant movement is illustrated in Fig. 9. This figure shows contaminant retardation during transport in a shallow ground water flow system. Typical values for the aquifer properties of porosity and hydraulic conductivity and for the values of transverse and longitudinal transmissivity were used in the computations on which this figure is based. A transport time of 60 years was used. The $K_l = 0$ case illustrates contaminant transport in a homogeneous, isotropic aquifer where no adsorption takes place.

As K_l values increase, the portion of the flow domain containing contaminant at a concentration greater than 10% of the initial contaminant concentration becomes smaller and smaller. For K_l values orders of magnitude greater than 1 mL/g, the contaminant is essentially immobile. The K_l values obtained from the "unmodified pH" AP and B3t horizon soil adsorption isotherms suggest, when viewed in light of the information presented in Fig. 9, that PCP is relatively immobile in Missouri soils compared to nonreactive solute species. An evaluation of PCP transport based on the linear adsorption coefficients determined in this study and using an available computer transport model would give a more exact description of PCP retardation in ground water flow.

The results of this study to indicate, however, that while PCP may undergo significant adsorption to soil, the adsorption is, to a great extent, reversible.

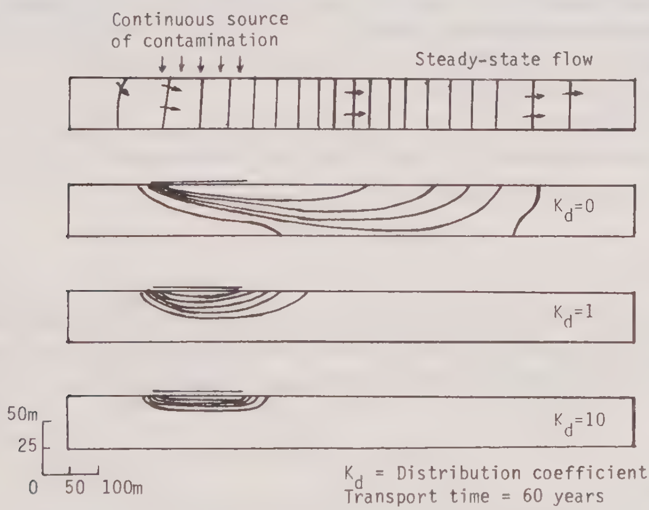

FIG. 9—*Effect of the linear adsorption coefficient* K_l ($K_l = K_d$) *on contaminant retardation during transport in a shallow ground water flow system from Freeze and Cherry* [18].

To discuss the implications of this reversibility on PCP transport in ground water, a simple hypothetical case of aquifer contamination will be used.

It will be assumed that a steady stream of PCP contaminated water enters a shallow aquifer for a limited period of time. Convective transport will carry the PCP contaminated plume in the general direction of ground water flow, but adsorption will significantly retard the advance of the plume as compared to the flow of the ground water (as in Fig. 9). The assumption is that the input of PCP into the aquifer is stopped. As the input of contaminant mass into the system is discontinued, some of the adsorbed contaminant will return to the water phase as lower concentration water flushes through the previously contaminated zone.

The results of this study suggest that PCP adsorption to soil will not permanently remove PCP from a contaminant plume but will rather act to retard and dilute its concentration. PCP, in a heavily contaminated plume, may temporarily partition onto the soil phase, but will then slowly be released to the water phase when ground water of a lesser PCP concentration passes through the soil.

Conclusions

Following conclusions were made on the basis of the experimental results:

1. Adsorption of PCP to soils can be accurately described by the Freundlich relationship over the concentration range studied.
2. While the organic matter content of a soil is important in determining the extent of adsorption, an additionally important soil property is pH.
3. Adsorption of PCP to soils increases significantly with decreasing pH.
4. Adsorption coefficients obtained in batch adsorption experiments indicate significant retardation of a PCP contaminant plume will occur during ground water flow through the soil.
5. Adsorption of PCP to soils is, to a large extent, a reversible process, indicating that adsorbed PCP will slowly be released when ground water of lower PCP concentration passes through the soil.

Acknowledgments

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Sorption Kinetics of Competing Organic Substances on New Jersey Coastal Plain Aquifer Solids

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REFERENCE: Uchrin, C. G. and Katz, J., **"Sorption Kinetics of Competing Organic Substances on New Jersey Coastal Plain Aquifer Solids,"** *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 140–150.

ABSTRACT: Batch rate and equilibrium experiments were conducted to examine the sorption characteristics of a mixed solute system consisting of para-dichlorobenzene (*p*-DCB) and 2,4-dichlorophenol (2,4-DCP) to solids from two New Jersey coastal plain aquifer systems. Results were compared to previously reported results obtained for single solute systems. The *p*-DCB effected a slight enhancement on the 2,4-DCP sorption to the Potomac-Raritan-Magothy (PRM) aquifer solids rather than an inhibitory effect. This was also noted for the adsorption of *p*-DCB on the Cohansey aquifer solids in the presence of 2,4-DCP. The other systems (2,4-DCP on the Cohansey aquifer solids in the presence of *p*-DCB and *p*-DCB on the PRM aquifer solids in the presence of 2,4-DCP) exhibited indiscernable competitive effects. The aquifer solids with the larger organic content adsorbed more of each substance. The data obtained using the more homogeneous aquifer solids evidenced less scatter.

KEY WORDS: adsorption, aquifers, ground water, competitive adsorption, para-dichlorobenzene, sorption, 2,4-dichlorophenol

Many mathematical models of pollutants in porous media include a reaction term to account for not only chemical and biochemical reactions but also sorption kinetics. Certain organic substances tend to be rather nonreactive but are hydrophobic and can associate quite readily to solid particulates. Other substances can be strongly attracted to functional groups that may be present on the solids. Knowledge of a pollutant's sorptive characteristics in a

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particular solute-sorbent system is critical to prediction of its transport and fate in ground as well as surface water systems.

In many cases, the danger to aquifer systems comes not from a pure substance spill or leak but from a "soup" of various organic substances, an example being landfill leachate. To date, work reported in the literature on competitive, or multi-solute, adsorption has been focused on organic substance removal by activated carbon [*1–4*] and on the sorption of various inorganic ionic species on soils and clays as reported by Murali and Aylmore [*5–7*]. Very little work, however, has been reported on the sorption of multiple organic substances on soils, clays, and sediments [*8,9*]. This paper presents research results from laboratory studies examining the competitive adsorption of para-dichlorobenzene (*p*-DCB) and 2,4-dichlorophenol (2,4-DCP) to solids obtained from two New Jersey Coastal Plain aquifer systems.

Procedure

Aquifer Solids

Solids from two New Jersey coastal plain aquifers were used in this study. The Cohansey aquifer material was taken from an outcrop located at the Rutgers University Cranberry Culture Experiment Station near Chatsworth, NJ. The Potomac-Raritan-Magothy (PRM) material was obtained from an excavation site located near Princeton, NJ. Physical properties of the aquifer materials are given in Table 1. Organic content was determined by the Walkley and Black modification of the rapid dichromate oxidation technique [*10*], with organic carbon content defined as 58% of the organic matter content.

Rate Studies

A 5.00-g mass of air-dried solids was introduced into a series of 50-mL screw cap test tubes. One tube was kept free of solids as a control. The solids were then saturated with 2.5 mL of organic-free (containing no interferences

TABLE 1—*Aquifer solids: physical properties.*

Property, %	Cohansey Solids, %	Potomac-Raritan-Magothy Solids, %
Sand	90.0	70.4
Silt	8.0	24.0
Clay	2.0	5.6
Organic matter	4.4	2.2

with the compounds of interest) water. The tubes were then spiked with a 25.0-mL volume of a solution of known concentrations of *p*-DCB and 2,4-DCP in water. A carrier solvent was not used. The tubes were immediately sealed by screwing on Teflon®-lined caps and agitated by wrist shakers. Tubes were withdrawn at specific time intervals for analysis.

To determine the residual concentration, the tubes were centrifuged for 10 min at 2000 rpm to separate the solids. A 5.0-mL volume aliquot was then withdrawn from each vial and extracted with 5.0 mL of hexane and the extract analyzed using a Hewlett-Packard 5840-A gas chromatograph. A 1.83 m (6 ft) by 2 mm inside diameter (ID) column packed with 20% SP2100 (100/120 mesh) was used together with an electron capture detector. The resultant concentration versus time plots, displayed in Figs. 1 and 2, show that equilibrium conditions were reached for all systems within 24 h. Analysis of the blanks showed losses to volatilization and to the glassware to be less than analytical error and, thus, negligible. Analytical error was computed to be less than 3% based on an analysis of 15 replicates of known standards of the substances of interest.

Adsorption Equilibrium Studies

An identical procedure to the rate studies was employed except that a matrix consisting of different pollutant spike concentrations as well as different solid masses was examined and the agitation by wrist shakers was carried out until equilibrium was reached. In all, two equilibrium studies were performed

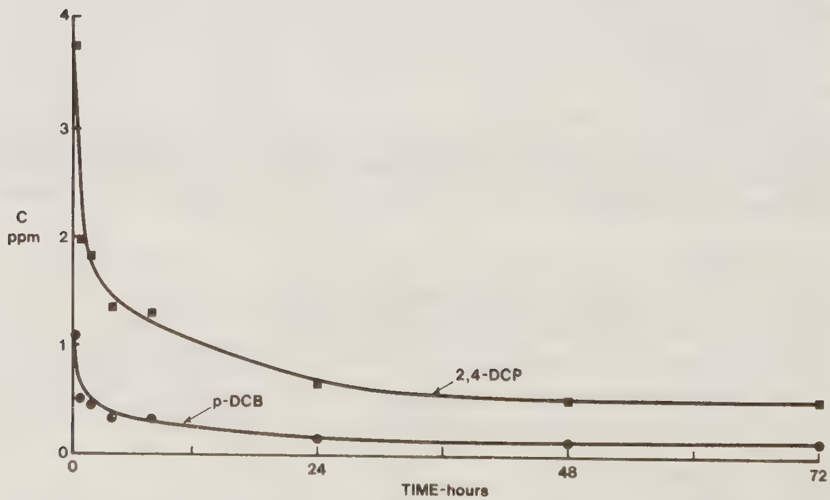

FIG. 1—*Dual solute batch adsorption rate study, para-dichlorobenzene (*p-DCB*) and 2,4-dichlorophenol (2,4-DCP) on Cohansey aquifer solids.*

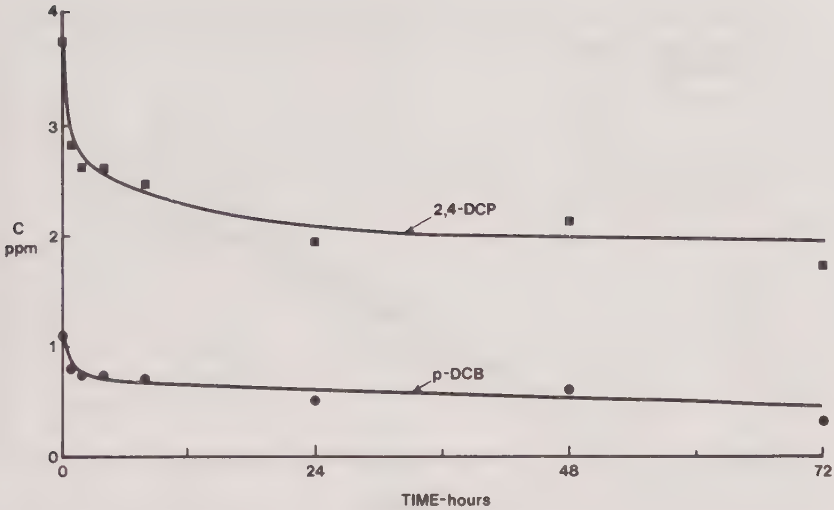

FIG. 2—*Dual solute batch adsorption rate study, para-dichlorobenzene (*p-*DCB) and 2,4-dichlorophenol (2,4-DCP) on Potomac-Raritan-Magothy (PRM) aquifer solids.*

on each aquifer material. In the first, the spike concentration of 2,4-dichlorophenol (2,4-DCP) was held constant (4.86 ± 0.38 ppm for the Cohansey solids and 3.84 ± 0.28 ppm for the PRM solids) while the spike concentrations of para-dichlorobenzene (*p*-DCB) were varied. In the second, the spike concentration of *p*-DCB was held constant (4.06 ± 0.40 ppm for the Cohansey solids and 4.15 ± 0.30 ppm for the PRM solids) while the spike concentrations of 2,4-DCP were varied.

All experiments were performed in a constant temperature room at 21 ± 1°C.

Results

Linear, Langmuir and Freundlich isotherms were fitted to the data. The Freundlich expression provided the best overall fit. This expression is given as

$$q_e = KC_e^{1/n} \tag{1}$$

where q_e is the solid phase equilibrium concentration (μg of organic substance/g of soil, or ppm), C_e is the liquid phase equilibrium concentration (mg of organic substance/L of water, or ppm), and n and K are constants. Figure 3 shows the Freundlich isotherm obtained for p-DCB on the Cohansey solids in the presence of a constant spike concentration of 2,4-DCP. Also included in this figure are results from a previous study [*11*] examining the

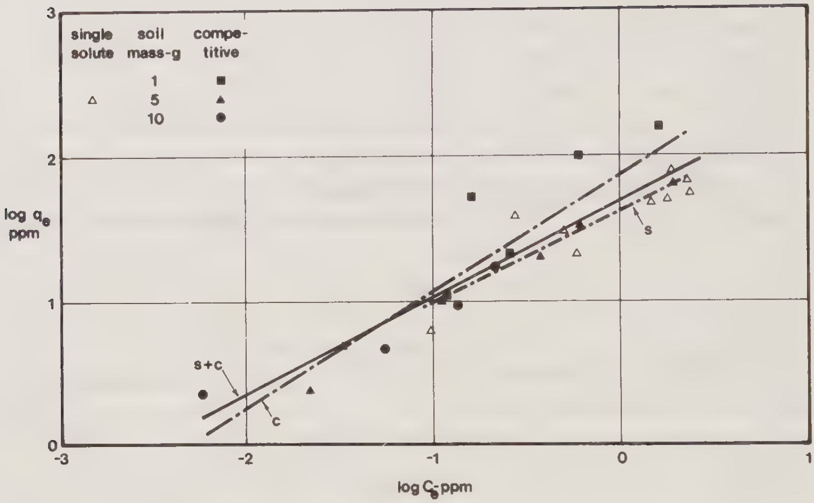

FIG. 3—*Freundlich adsorption isotherms for* p-*DCB on Cohansey aquifer solids. Trace (s) represents an isotherm regressed to the single solute data. Trace (c) represents an isotherm regressed to the competitive data, and Trace (s+c) represents an isotherm regressed to both data sets.*

sorptive behavior of *p*-DCB as a single solute on the same material. An initial observation is that there is no consistent relationship between the soil masses used in the experiments and isotherm parameters other than to increase the data scatter. Other studies [*12–16*] have been reported that have shown the adsorbent mass to affect the adsorption equilibrium characteristics, specifically the partition coefficient, for certain other organic substances, even though there is no fundamental intuitive basis for this effect. It is interesting to note that the isotherm for the competitive system (Trace c) exhibits a slightly greater net adsorption than the isotherm for the single solute system (Trace s) suggesting that the presence of the 2,4-DCP may have enhanced the adsorption of *p*-DCB. This phenomenon was addressed by Weber [*17*]. It should be noted that the difference between the isotherms is small, and a singular isotherm could be fitted to the data (Trace s + c), which is not significantly different (based on the regression analyses) than the separate isotherms for the single solute system and the competitive system. Freundlich isotherm parameters are given in Table 2.

The Freundlich isotherm for the 2,4-DCP/Cohansey aquifer solids system in the presence of a constant amount of *p*-DCB is displayed in Fig. 4. Again, a dependency on adsorbent mass is not observed, but in this case no difference is apparent between the competitive and the single solute systems. Thus, a singular isotherm represents the data well. Parameters are also given in Table 2.

TABLE 2—*Freundlich isotherm parameters, Cohansey solids.*

Substance/Mode	K	$1/n$	Correlation Coefficient, r
p-DCB/single solute (s)	40.5	0.618	0.894
p-DCB/comp. with 2,4-DCP (c)	73.0	0.804	0.916
p-DCB/singular isotherm (s + c)	48.7	0.665	0.908
2,4-DCP/singular isotherm	26.4	0.601	0.915

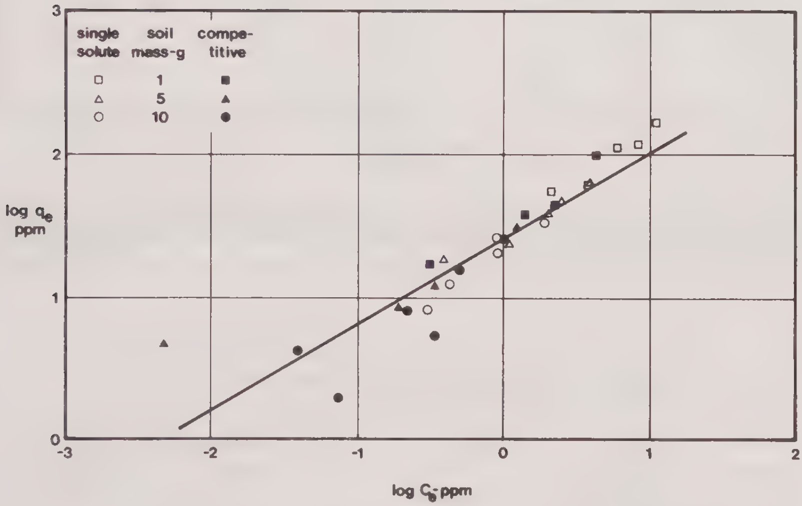

FIG. 4—*Freundlich adsorption isotherm for 2,4-DCP on Cohansey aquifer solids.*

Figure 5 displays the Freundlich isotherm for the p-DCB/PRM aquifer solids system in the presence of a constant amount of 2,4-DCP. There is a large degree of scatter in these data, which was typical of other sorption data obtained using this soil [*11, 15, 18*]. Since the same techniques were used as for the experiments with the Cohansey solids, analytical error cannot explain the scatter. A possible explanation is that the increased scatter may be due to the PRM material being more heterogeneous than the Cohansey (Table 1). This would be especially true of the experiments with the smallest adsorbent mass. It is difficult to determine whether a singular isotherm (Trace s + c) is more appropriate than individual isotherms for single solute (Trace s) and competitive systems (Trace c). Parameters for all are given in Table 3.

Finally, the Freundlich isotherm for the 2,4-DCP/PRM solids system in the presence of a constant amount of p-DCB is displayed in Fig. 6. The data

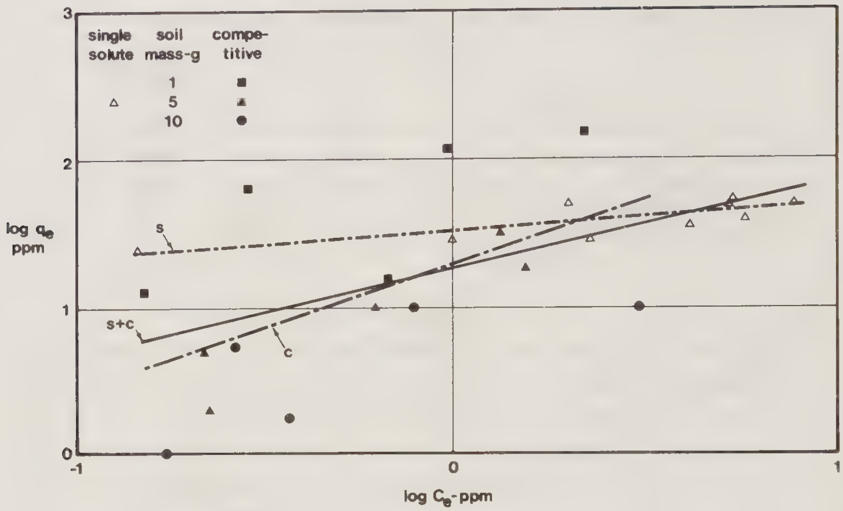

FIG. 5—*Freundlich adsorption isotherms for* p-*DCB on PRM aquifer solids. Trace (s) represents an isotherm regressed to the single solute data. Trace (c) represents an isotherm regressed to the competitive data, and Trace (s + c) represents an isotherm regressed to both data sets.*

TABLE 3—*Freundlich isotherm parameters, PRM solids.*

Substance/Mode	K	$1/n$	Correlation Coefficient r
p-DCB/single solute (s)	32.0	0.178	0.773
p-DCB/comp. with 2,4-DCP (c)	19.5	0.860	0.560
p-DCB/singular isotherm (s + c)	18.6	0.613	0.605
2,4-DCP/single solute (s)	8.3	0.247	0.382
2,4-DCP/comp. with *p*-DCB (c)	11.0	0.904	0.729
2,4-DCP/singular isotherm	8.2	0.404	0.502

are again typified by a large degree of scatter, but here it is apparent that there is a difference between the single solute isotherm (Trace s) and the mixed, competitive system (Trace c). It can be concluded that the adsorption has been enhanced in this system because of the presence of the second solute. Parameters for these isotherms together with the parameters for a singular isotherm describing all the data are given in Table 3.

The equilibrium data obtained for the substances held at fixed concentration are given in Tables 4 through 7. These data show that, in general, the spike concentration of the competing substance has little discernable effect on the equilibrium position of the other substance. Although the spike con-

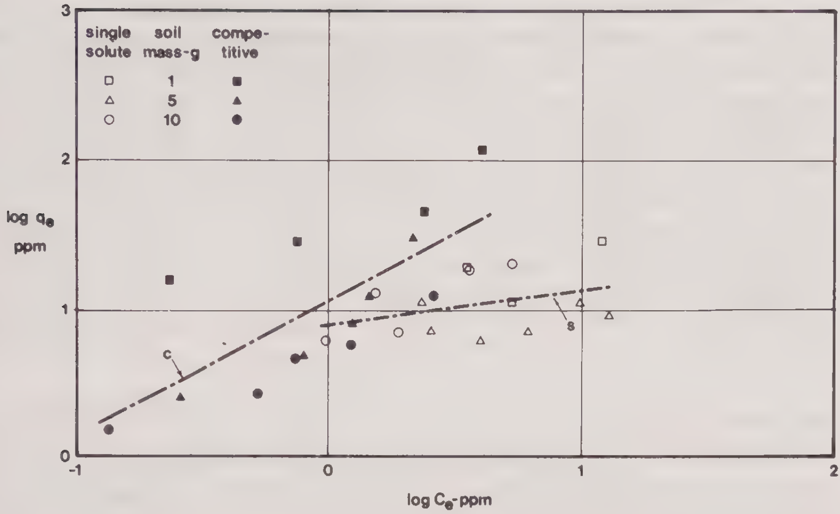

FIG. 6—*Freundlich adsorption isotherms for 2,4-DCP on PRM solids. Trace (s) represents an isotherm regressed to the single solute data and Trace (c) represents an isotherm regressed to the competitive data.*

TABLE 4—*Competitive adsorption equilibrium data, Cohansey solids.*

Spike Concentration p-DCB, ppm	Equilibrium Data, ppm — 2,4-DCP					
	Soil Mass = 1 g		Soil Mass = 5 g		Soil Mass = 10 g	
	C_e	q_e	C_e	q_e	C_e	q_e
7.49	2.00	81	0.425	22	0.190	11
4.34	1.87	90	0.485	23	0.233	11
2.08	1.78	83	0.468	21	0.172	10
1.02	1.58	97	0.452	23	0.202	11
0.53	1.57	85	0.507	21	0.208	10

TABLE 5—*Competitive adsorption equilibrium data, Cohansey solids.*

Spike Concentration 2,4-DCP, ppm	Equilibrium Data, ppm — p-DCB					
	Soil Mass = 1 g		Soil Mass = 5 g		Soil Mass = 10 g	
	C_e	q_e	C_e	q_e	C_e	q_e
7.69	0.589	94	0.439	18	0.257	8.6
3.80	1.21	80	0.579	35	0.241	8.7
2.76	1.48	68	0.476	17	0.476	7.7
1.86	1.37	71	0.469	17	0.234	8.3
0.94	2.21	56	0.507	20	0.620	8.9

TABLE 6—*Competitive adsorption equilibrium data, PRM solids.*

Spike Concentration p-DCB, ppm	Equilibrium Data, ppm — 2,4-DCP					
	Soil Mass = 1 g		Soil Mass = 5 g		Soil Mass = 10 g	
	C_e	q_e	C_e	q_e	C_e	q_e
7.71	2.73	39	1.54	12	1.45	5.5
5.23	2.57	41	1.69	11	1.31	5.7
2.68	2.61	36	1.59	11	1.43	5.1
1.21	2.49	41	1.48	12	1.40	5.3
0.61	2.40	41	1.69	10	1.51	4.8

TABLE 7—*Competitive adsorption equilibrium data, PRM solids.*

Spike Concentration 2,4-DCP, ppm	Equilibrium Data, ppm — p-DCB					
	Soil Mass = 1 g		Soil Mass = 5 g		Soil Mass = 10 g	
	C_e	q_e	C_e	q_e	C_e	q_e
8.11	2.21	55	1.25	14	1.47	5.7
3.85	2.19	54	1.66	12	1.46	5.6
2.72	. . .	. . .	1.99	11	1.26	6.5
1.73	2.04	61	2.12	10	1.51	5.8
0.79	1.91	69	2.12	11	1.54	6.0

centration range employed was small, these results support the case for singular isotherms to describe the sorptive characteristics of the less demonstrative systems.

It is also of interest to note that in all cases, the Cohansey solids adsorbed more of each substance than the PRM solids. Since the Cohansey material has a higher organic matter content and a concomitant organic carbon content than the PRM material, these findings support the work of other investigators [*4,19,20*] who have identified the organic carbon fraction as a controlling factor for predicting solute/water/soil partitioning coefficients.

It can also be deduced from the Freundlich isotherm exponents, $1/n$ that the adsorption evidenced by these systems is "favorable" [*17*]. Additional studies [*11*] examining the desorption of p-DCB and 2,4-DCP from these soils have demonstrated a significant resistance to release, which suggests that the nature of the sorptive processes for these systems is more chemisorptive than physical [*21*].

Summary

Batch experiments were conducted to examine the sorption characteristics of a mixed solute system consisting of p-DCB and 2,4-DCP to solids from two

New Jersey coastal plain aquifer systems. Results were compared to previously reported results obtained for single solute systems. The presence of p-DCB did not affect the adsorption of the 2,4-DCP to the Cohansey material. A slight enhancement effect was noted for the system examining the adsorption of 2,4-DCP on the Cohansey material in the presence of p-DCB. Data scatter in the system examining the adsorption of p-DCB on the PRM solids in the presence of 2,4-DCP did not allow for a definitive conclusion. Finally, the adsorption of 2,4-DCP to the PRM solids was demonstrably enhanced by the presence of the p-DCB. The degree to which the adsorption of one substance was enhanced, however, was not shown to be a function of the amount of the other substance.

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Contents of this publication do not necessarily reflect the views and policies of the U.S. Department of the Interior, nor does mention of trade names or commercial products constitute their endorsement or recommendation for use by the U.S. Government.

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Principles of Bioreclamation of Contaminated Ground Water and Leachates

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ABSTRACT: Improper disposal of hazardous wastes has resulted in contamination of saturated and unsaturated subsurface materials (the soil/rock/ground-water system) and production of leachates. One of the least appreciated and least applied remedial treatment techniques for these contaminated materials is biological treatment. Such treatment can result in the destruction of hazardous contaminants and may be cheaper than other alternatives. Efficient bioreclamation can occur when a proper, uniform environment for the bacteria, adequate contact between the contaminated materials and the bacteria, and sufficient time to effect the degradation are provided. Maintaining the proper environment (aerobic, anaerobic, or both) includes making sure biodegradable organics are present in sufficient quantity, paying attention to microbial nutrition, keeping the pH in a suitable range, and ensuring that the bacteria can adapt to the presence of toxic substances. Selection of the bioreclamation technique to be used depends on the nature and concentration of the contaminants. The choices for above-ground treatment are suspended-growth and attached/entrapped-growth reactors. Attached/entrapped-growth systems have significant advantages for treating hazardous wastes. The three basic options for in-situ treatment are (1) enhancement of indigenous bacteria, (2) extraction-injection-recycle, and (3) creation of a biologically active barrier. Patience and an appreciation for the keys to efficient biological treatment are required to make these options work.

KEY WORDS: bioreclamation, biological treatment, contaminated ground water, ground water, hazardous wastes, in-situ treatment, leachates

Various estimates indicate that from 40 to 100 million metric tons of haz-

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ardous waste are generated yearly in the United States. Improper disposal of these materials has resulted in contamination of saturated and unsaturated subsurface materials (that is, the soil/rock/ground-water system) and production of leachates. One of the least appreciated and least applied remedial treatment technology for these contaminated materials is biological treatment. The major potential advantages of bioreclamation of contaminated soils and ground waters, and leachates are that it is relatively inexpensive compared to other reclamation techniques and it converts hazardous materials to nontoxic end products. To assess the feasibility of bioreclamation, one must determine if the organics present are biodegradable and if potential toxic substances are present at adversely high concentrations. The purpose of this paper is to provide information that will convince environmental engineers and scientists that bioreclamation is an appropriate treatment technology for soils and waters contaminated with hazardous substances.

Requirements for Bacterial Growth

When assessing the feasibility of bioreclamation of contaminated ground waters and leachates, it is useful to develop a "check list" of requirements for bacterial growth that will provide the framework for the evaluation. If existing conditions meet or can be made to meet these requirements, bioreclamation will be feasible.

Carbon and Energy Source

There must be a biodegradable organic compound present to sustain bacterial growth. The pollutant itself may be biodegradable and serve as the carbon and energy source. Pollutants may also be transformed to nontoxic end products by processes called secondary utilization and cometabolism [*1–3*]. Here, another organic serves as the primary energy source while pollutants are transformed without contributing significantly to bacterial energy production or growth. The primary energy source may already be present in the contaminated water or it may need to be added [*4*]. To determine if the organics present are degradable under aerobic conditions, the standard biochemical oxygen demand (BOD) test [*5*] or a modified BOD test (to account for the possible presence of toxic substances [*6*] can be used. For some organics, for example, hydrocarbons, acclimated bacteria should be used since the typical BOD seed may not contain significant populations of organisms capable of degrading atypical organics. In such cases, long-term biodegradation tests may be required. The method described by Owen et al. [*7*] can be used to assess anaerobic degradability. It should be stressed that analysis for

chemical oxygen demand (COD) or total organic carbon (TOC) will not determine biodegradability. These analyses will only determine if organic matter is present. However, a reduction in these parameters during biodegradation experiments may be used to indicate the presence of biodegradable materials.

In general, contaminants must be dissolved in the water for bacteria to accomplish biotransformation. However, this does not mean that so-called "nonaqueous phase liquid" (NAPL) contaminants cannot be degraded. As long as there is an aqueous second-phase interface, bacteria can act on the NAPL materials dissolved in the water. Since solubility in water is an equilibrium, as soluble contaminants are removed from aqueous solution by bacteria, more of the second-phase liquid dissolves in water and the reaction continues. It has been shown that biotransformation rates can be increased by increasing the interfacial area between the second-phase liquid and water [*8,9*]. This property of biological growth may be particularly important for sites where there seems to be an abundance of second-phase liquids (for example, gasoline). Of course, the first step in such a reclamation project may be recovery of free NAPL materials.

It should be noted that unless the hazardous organics are completely mineralized during biodegradation, the degradation products may also be toxic. For example, it has been shown that under some conditions, trichloroethylene can be biotransformed into vinyl chloride [*4*].

Electron Acceptor (Nature of the Environment)

The importance of the electron acceptor is manifested by the difference in susceptibility of pollutants to biotransformation (conversion to end products) in different environments. In aerobic environments, oxygen is the electron acceptor; in anoxic environments, it is nitrate; and in anaerobic environments, sulfate, carbon dioxide, or reduced organics (mostly acetic acid) serve as electron acceptors. For example, most chlorinated benzenes are degradable aerobically, but not under anoxic or anaerobic conditions [*2,4*]. Some chlorinated aliphatics (like chloroform) are degradable anaerobically, but not aerobically [*2,4*]. At the present time, very few hazardous pollutants have been shown to be degradable only under anoxic conditions [*2,4*]. Thus, it is imperative to know the nature of the electron acceptor to determine which, if any, method of bioreclamation is feasible.

If oxygen is to be the electron acceptor, it will have to be added either above or below ground. Aeration can be a significant operational expense. To maximize hazardous pollutant biotransformation, it is at this time recommended that nitrate not serve as the electron acceptor since, as described above, few hazardous pollutants have been shown to be degradable under these conditions. It may, however, be beneficial to create an anaerobic environment to enhance bioreclamation. This will be discussed in a subsequent section.

Macronutrients

There must be sufficient nitrogen, phosphorus, and sulfur (the anaerobic requirement for sulfur is greater than the aerobic requirement) to insure these nutrients do not limit biotransformation of pollutants. Nitrogen can be present as ammonia, nitrite, nitrate, or organic nitrogen (for example, amino acids). Phosphorus is generally needed as orthophosphate, with sulfur as sulfate for aerobic environments and sulfide for anaerobic environments. With anaerobic bacteria, the sulfur requirement may be as high as the phosphorus requirement [*10*]. If these constituents are not present in sufficient quantities, they must be added.

Micronutrients

Trace metals (potassium, iron, molybdenum, zinc, and so forth) are the major concern here and are needed in the 0.01 to 5 mg/L range. Iron and nickel are particularly important for anaerobic bacteria [*10*]. While some trace organics (for example, amino acids and vitamins) may be beneficial, they very rarely need to be added. Addition of a mixture of trace organics and metals, such as yeast extract, may be helpful in acclimating a bacteria culture to the contaminated soil or water.

Proper pH

As long as pH is in the range of 6.5 to 8.5, biological activity will not be significantly affected. When organic concentrations are high (>500 mg/L), alkalinity may be required (typically accomplished by adding lime) if the nature of the organics is such that acids are produced as intermediate products during biodegradation. Addition of alkalinity guards against pH drops that may adversely affect biological activity and may be particularly important during the acclimation and start-up process.

Temperature

Biological reaction rates increase with increasing temperature. Temperature may be very critical for anaerobic environments; 30 to 35°C is generally considered to be optimal. However, anaerobic biotransformations will take place at 15 to 25°C providing sufficient time is provided. Below 5°C, most biological activity virtually ceases. Aerobic biotransformations will not be temperature limited as long as the temperature is 20°C or above. Biotransformations will occur at lower temperatures; however, since rate of bioconversion is reduced, more time will be required.

Absence of Toxic Materials

Whether a material is toxic or not is a function of the nature of the material, its concentration, and the ability of microorganisms to acclimate to its presence. The keys to acclimation are providing a proper mix of bacteria and sufficient time for the bacteria to acclimate. Organic pollutants that are initially toxic may become primary carbon and energy sources or secondary substrates given sufficient time (usually called lag time) [*2,4,11*].

At trace concentrations (nominally defined as <1 mg/L), many organics can be biotransformed via secondary utilization [*2,4*]. In the "intermediate" concentration range, hazardous organics may be biotransformed as primary substrates. The magnitude of this range is not well defined, but is believed to be approximately 1 to 100 mg/L. However, some organics are biodegradable at much higher concentrations. Phenol, a hazardous organic, has been shown to be anaerobically degradable at concentrations near 2000 mg/L [*12*]. At very high concentrations, the organics are toxic to the bacteria and no biotransformation will occur. Other pollutants, such as heavy metals, cannot serve as primary or secondary substrates, but bacteria can acclimate to reasonably high concentrations (greater than 100 mg/L) under the proper conditions [*13*].

An additional concern is the effect of combinations of various toxicants. Combinations can be synergistic (worse than summed individual effects) or antagonistic (less severe than summed individual effects) [*14*]. Since the number of combinations is infinite, possible synergism or antagonism must be evaluated on a case by case basis.

Adequate Contact

To ensure efficient biotransformation, there must be efficient and adequate contact between the contaminated water and the bacteria. With above-ground treatment, this means sufficient mixing with suspended-growth reactors (water and bacteria homogeneously mixed) and uniform flow distribution with attached/entrapped-growth reactors (bacteria attached to some surface or trapped in some manner within the reactor; for example, held in the void space). With below-ground treatment, adequate contact is much less straightforward. Either bacteria, contaminants, or nutrients must be distributed relatively uniformly throughout the subsurface using a series of injection wells, or by directing contaminated water to flow uniformly (by taking advantage of the natural gradient or by pumping/injection) through a zone (similar to a slurry trench) containing the bacteria. Obviously, control of biotransformation is much easier with above-ground methods; however, below-ground methods may be cheaper if uniform contact can be created.

The hydrogeologic setting of some sites may be favorable for downward contaminant transport from the unconsolidated overburden materials (flow

through porous media) into the underlying bedrock. These contaminants may then be transported through joints, solution channels, or other discontinuity in the bedrock mass (fracture flow). The natural condition may be further aggrevated by inducing a downward gradient by pumping or injection to produce a ground-water divide. In either case, it may be difficult to ensure adequate contact between bacteria and contaminants during in-situ, subsurface treatment.

Sufficient Time

Perhaps the most important key to efficient bioreclamation is providing adequate time for the bacteria to effect the biotransformation. Specifically, sufficient bacterial solids retention time (SRT), to be distinguished from liquid or hydraulic retention time (HRT) is required. Pollutant removal rate can be expressed as the mass of pollutant removed per day per mass of bacteria. The larger the bacterial mass, the greater the biotransformation rate. In addition, maintaining a longer bacterial retention time maximizes the potential for acclimation to resistent organics and potential toxicants. Thus, the take-home message for bioreclamation of contaminated soils and ground waters and leachates is to keep all the bacteria you grow.

With above-ground treatment, SRT is provided by tank volume and biomass recycle via sedimentation in suspended-growth reactors and by attachment to surfaces or entrapment or both in attached/entrapped-growth reactors. The key to economic biotransformation is providing large SRTs (high efficiency) at low HRTs (capital cost) [*15,16*]. Attached/entrapped-growth systems offer significant advantages in this regard.

In-situ treatment offers the potential of the long SRTs needed for acclimation and efficient biotransformation. Since the soil provides the surface, attached growth and entrapment will occur. The main problem here would be ensuring adequate contact as described above.

With the above described "check list" as a basis, the feasibility of bioreclamation can be evaluated once the nature of the contaminants is known.

Assessing Potential for Bioreclamation

The feasibility of bioreclamation of contaminated soils and ground waters and leachates can be addressed by discussing the biodegradability and toxicity of specific contaminants, the potential for synergism and antagonism of the mixture of components, and the importance of other environmental factors and good laboratory studies.

Biodegradability and Toxicity of Organics

When considering the bioreclamation of soils and waters contaminated with organics, two questions must be addressed:

1. Are the organics biodegradable as primary or secondary substrates?
2. At what concentrations are the organics toxic?

The following discussion will focus on general organics and then on chlorinated organics, since these chlorinated compounds seem to be present in many of the contaminated soils and ground waters and leachates.

General Organics—Almost all organics are biodegradable; however, the rate and extent of degradation vary widely. Rate and extent of biodegradation have been shown to be a function of concentration, molecular structure, and a variety of environmental factors [*1–20*]. The following is a partial list of organics that have been shown to be degradable under both aerobic and anaerobic conditions along with some specific example compounds [*1,3,8,20–27*]:

- Acids (acetic, benzoic)
- Amines (dimethyamine, urea)
- Benzenes (benzene, styrene)
- Ketones (acetone)
- Phenolics (phenol, catechol, *p*-cresol)
- Cyanide
- Starches
- Proteins
- Alcohols (ethanol, ethylene glycol)
- Aldehydes (formaldehyde)
- (DDT)
- Nitrobenzene
- Sugars
- Fats
- Many, many others

The effect of concentration can be demonstrated by considering the anaerobic degradation of phenol as an example [*12*]. Phenol is inhibitory to unacclimated bacteria at a level of about 500 mg/L. However, with acclimation, phenol can be degraded at a concentration of about 2000 mg/L. The "nature" of an organic can be changed from toxic to nontoxic to biodegradable with careful attention to the fundamentals of biodegradation as described under Requirements for Bacterial Growth.

Chlorinated Organics—Chlorinated organics are treated separately here because of their ubiquitous presence in contaminated soils and ground waters and leachates and the widely perceived notion that they are *very* toxic and nondegradable. It has been shown that many chlorinated organics can serve

TABLE 1—*Reported relative biodegradability of selected chlorinated organics under aerobic, anaerobic, and anoxic conditions.* [a]

Contaminant	Is the Contaminant Degradable? [b]		
	Aerobic	Anaerobic	Anoxic
Methylene chloride	yes	yes	no
Chloroform	no	yes	no
Carbon tetrachloride	no	yes	yes
Trans 1,2-dichloroethylene	no	yes	? [c]
1,1,1-Trichloroethane	no	yes	no
1,1,2-Trichloroethane	no	yes	no
1,1,2,2-Tetrachoroethane	no	yes	no
Tetrachloroethylene	no	yes	no
Trichloroethylene	no	yes	no
Vinyl chloride	no	yes	no
Chlorobenzene	yes	no	no
1,2-Dichlorobenzene	yes	no	no
1,3-Dichlorobenzene	yes	no	no
1,4-Dichlorobenzene	yes	no	no
1,2,4-Trichlorobenzene	yes	no	no
Pentachlorophenol	yes	yes	? [c]

[a] Adapted from Refs *2,4,21,22,25,26,28–34.*

[b] Not all compounds listed have been tested as both primary and secondary substrates. Just because yes or no is listed does not mean that the compound has been studied exhaustively and that the "final" answer has been found.

[c] The compound has not been tested under this condition.

as both primary and secondary substrates [*2,4,21,22,25,26,28–34*]. Table 1 contains a partial list of compounds that have been found to be degradable under aerobic, anaerobic, and anoxic conditions. It has been reported that, in general, chlorinated aliphatics (for example, chloroform and trichloroethylene) are biotransformed under anaerobic conditions but not aerobically, while chlorinated aromatics (for example, the chlorobenzenes) are degraded aerobically but not anaerobically. However, it should be pointed out that some exceptions have been reported (for example, methylene chloride [*28,29*] and pentachlorophenol [*30–32*]. Much research needs to be done to expand and clarify this list.

For the most part, data contained in the literature are incomplete at best and in many cases misleading. For example, in many of the reports, it is not clear whether removal is by volatilization (stripping), adsorption onto the organic solids or by biodegradation. Also not reported in general is the ability of bacteria to acclimate to many of the compounds and change the "definition" of the candidate organic from toxic to biodegradable.

The effect of concentration has not been clearly defined. At low concentrations, chlorinated organics can serve as secondary substrates. At intermediate concentrations, chlorinated organics can be toxic to unacclimated bacteria

and serve as primary substrates for acclimated bacteria. At high concentrations, chlorinated organics are toxic. The concentration ranges where these compounds are secondary and primary substrates and toxic are not well understood at the present time. For example, chloroform serves as a secondary substrate at 20 to 100 μg/L [*2,4*]. It may be toxic to unacclimated anaerobic bacteria at 0.5 mg/L, but these organisms can acclimate to at least 40 mg/L [*35*]. At the present time, very little is known about the upper limit of the acclimation range. For example, it has been reported that aerobic bacteria can handle up to 200 mg/L of methylene chloride [*21*], but a similar number has not been developed for anaerobic bacteria. This does not mean that anaerobic bacteria can not handle these levels of methylene chloride; at the present time, 10 mg/L is the highest level tested [*28*].

Toxicity of Inorganics

Many inorganics may be present in contaminated soils and ground waters and leachates at levels that are considered to be "hazardous." A partial list is given below:

- Salts (ionic strength)
- Sulfate
- Light metal cations (sodium, potassium, calcium, and magnesium)
- Heavy metals (for example, cadmium, chromium, copper, iron, mercury, nickel, lead, and zinc)
- Sulfide
- Ammonia-N(NH_4^+ and NH_3)

Few inorganics are biotransformed or metabilized to any extent (some important exceptions are nitrification of ammonia and sulfate reduction to sulfide). Inorganics, such as heavy metals, can be sorbed onto bacteria. However, in general, the mechanism of acclimation to inorganics will be different than for organic toxicants. However, bacteria can adapt to the presence of relatively high concentrations of a wide variety of toxic inorganics. For example, a total nickel concentration of about 50 mg/L is toxic to unacclimated methanogenic bacteria [*13*]. However, these organisms can acclimate to the presence of 250-mg/L total nickel given sufficient acclimation time (it should be noted that it is commonly believed that it is the soluble, free nickel ion that is toxic).

Potential for Synergism and Antagonism

With a mixture of many contaminants, as will generally be the case, the potential exists for synergism (making the toxicity more severe) or antagonism (making the toxicity less severe); synergism is much more likely. Although an individual toxic organic may be biotransformable at a given concentration, when combined with other potential toxicants, it may effectively

change from being biodegradable to nonbiodegradable or toxic. For example, if the maximum tolerable concentration of chloroform was 50 mg/L and for methylene chloride was 20 mg/L and if the compounds were present individually, they would be synergistic if when combined, the maximum tolerable concentrations were reduced to 20 and 10 mg/L, respectively. In addition, a nontoxic concentration could be changed to a toxic concentration via synergism. All contaminants (that is, general organics, chlorinated organics, and inorganics) may contribute to synergistic effects. Since the number of possible combinations is infinite, the only way to evaluate a given mixture is to test its degradability under well-controlled conditions in the laboratory.

Other Factors

A "check list" of requirements for bacterial growth was presented earlier. Since the primary goal of bioreclamation is to transform hazardous organics into nonhazardous end products, conditions must be developed such that nothing else limits or interferes with this transformation. If aerobic conditions are desired, sufficient oxygen must be provided; if anaerobic conditions are desired, air must be specifically excluded. Sufficient macronutrients and micronutrients (nitrogen, phosphorus, sulfur, iron, trace metals, and so forth) must be present. If not present in sufficient quantities, these materials will have to be added. For the most part, temperature is not expected to be a major problem. pH control may be necessary, especially during startup of the process. There must be adequate contact between the bacteria, contaminants, and nutrients. Finally, sufficient time must be provided to acclimate and biotransform the target contaminants. This should be provided with proper engineering design and operation.

To summarize, the major questions to be addressed before a definitive conclusion regarding bioreclamation feasibility can be drawn include:

1. Is the organic material biodegradable?
2. Does the mixture of individual components reduce the overall biodegradability?
3. What is the extent of the potential toxicity?
4. Are there sufficient nutrients available to support bacterial growth?

These questions can be answered by relatively simple analyses and laboratory studies. The time required for these studies depends upon the answers sought. Comprehensive aerobic degradability/toxicity studies may take 3 to 6 weeks, while similar anaerobic degradability/toxicity studies may take up to three months or more. However, the data obtained are necessary if a sound decision is to be made concerning the feasibility of bioreclamation. It needs to be emphasized that if the answer to Question 1 is no, bioreclamation will not be feasible.

Possible Management Alternatives

Once it has been determined that biodegradable material is present, the method of bioreclamation must be selected. If in-situ bioreclamation is selected, the decision is whether to treat the entire site or only specific areas. If above-ground treatment is selected, a pumping scheme must be devised and a choice between aerobic or anaerobic treatment and suspended-growth or attached/entrapped growth made. These aspects will be discussed below.

Selection of Waters/Areas to be Treated

Contaminated ground waters and leachates can be treated above-ground or in-situ. When assessing above-ground bioreclamation, an evaluation of an appropriate pumping scheme must be made. If a significant portion of the organic material is biodegradable, it may be advantageous to combine contaminated waters with relatively uncontaminated waters, providing dilution and reducing potential toxicity (for example, from chlorinated organics, heavy metals, salts, and so forth). Judicious selection of a pumping scheme can also provide biodegradable organics for areas that contain low levels of toxic organics, thus allowing biotransformation of the toxic organics as secondary substrates.

When evaluating in-situ bioreclamation, the decision is whether to treat the entire site or selected areas. The criteria involved in such a selection are whether biodegradable organics are present and whether potential toxic substances are present at adversely high concentrations. If low levels of toxic organics are present, a primary substrate may need to be added to allow for secondary utilization of the toxic organics. If concentrations of toxic materials are too high, other remediation techniques will be required for those areas.

An additional consideration for both management alternatives described above is downward migration of contaminants. Such migration needs to be addressed in light of the overall goals of remediation.

Above-Ground Bioreclamation

Above-ground treatment can be aerobic or anaerobic, suspended-growth, or attached/entrapped growth.

Aerobic Versus Anaerobic Bioreclamation—The difference between aerobic and anaerobic bioreclamation is the nature of the electron acceptor. In general, if a compound is degradable aerobically, it can be degraded anaerobically. However, as noted previously, with hazardous organics, there are some important exceptions. Chlorinated aromatics may be degradable aerobically but not anaerobically and chlorinated aliphatics may be degradable

anaerobically but not aerobically. However, those compounds not degradable aerobically may be removed by stripping (volatilization) during aeration. Thus there may be very little difference between overall removals of chlorinated aliphatics by anaerobic and aerobic treatment.

A disadvantage of aerobic treatment is that oxygen must be supplied, representing a significant operational expense. Aerobic growth results in the production of large amounts of bacterial sludge (in a typical aerobic process, approximately half the incoming organic matter is converted to bacteria). Anaerobic bacteria are slower growers than aerobic bacteria, producing only 10 to 20% as much bacterial sludge, and may thus require a longer SRT to accomplish equivalent removals. These longer SRTs can be obtained economically using attached/entrapped-growth reactors (sometimes called immobilized-cell reactors).

Attached/Entrapped Versus Suspended Growth—The basic difference between these two types of reactors is that with attached/entrapped-growth systems (AEG), a surface is provided for bacterial attachment and entrapment (rocks, plastic, sand, granular activated carbon, aluminum, or silicon oxides; media may either be static or fluidized (Fig. 1), or the reactor is operated in a manner that retains biomass (upflow sludge blanket or baffled reactors (Fig. 2), while with suspended-growth systems (SG), bacteria are kept in suspension by mixing. In typical SG systems, a settling basin is required following the bioreactor to settle the bacteria for recycle back to the bioreactor (Fig. 3). Detailed descriptions of these types of reactors are presented elsewhere [*15,16*].

The key to economical, efficient, above-ground, bioreclamation is separation of SRT (determines process efficiency and degree of acclimation) and HRT (determines capital cost). In this regard, AEG systems offer a significant advantage with their inherent solids retention capabilities. This is particularly critical in bioreclamation of contaminated ground waters and leachates since time is required for acclimation to resistant and toxic contaminants to occur. With SG systems, SRT is provided by a large reactor plus a sedimentation basin and sludge recycle pump. The trade-off is basically media cost versus settling tank and sludge pumping. It is difficult to economically obtain SRT levels much above 25 to 50 days with SG systems. AEG systems typically give SRT values in excess of 100 days. Since AEG systems can maintain higher biomass levels, they can operate at lower HRTs (for example, 0.5 to 2 h versus 3 to 10 h for SG). The magnitude of the required HRT will to a certain degree also be a function of the degradability of the organics. A potential advantage of aerobic SG systems is more efficient stripping of nondegradable, volatile organics.

Process efficiency for both AEG and SG systems is a function of SRT and the biodegradability of the organics. It is difficult to predict removal efficiencies without knowing rates of biodegradability. For example, in aerobic SG systems fed glucose, a readily degradable organic, 99% conversion can be

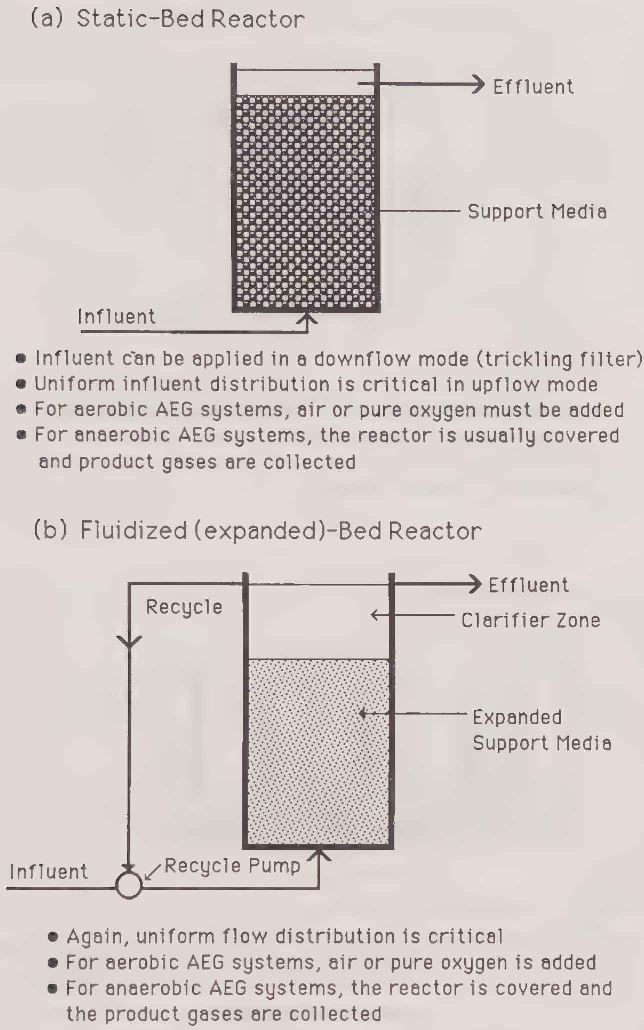

FIG. 1—*Attached/entrapped-growth reactors.*

accomplished with SRTs of 2 to 5 days and HRTs of 1 to 3 h. However, with hazardous organics like chlorobenzene, SRTs of greater than 50 days and HRTs of 10 to 24 h may be necessary to accomplish 99% conversion if indeed 99% conversion is kinetically possible. Again, the key is acclimation. With an acclimated culture in an AEG reactor, 99% conversion may be possible in less than 1 h.

It is easier to develop and maintain an acclimated culture with an AEG reactor. (Coincidentally, this may be why soil microbes operate so efficiently-

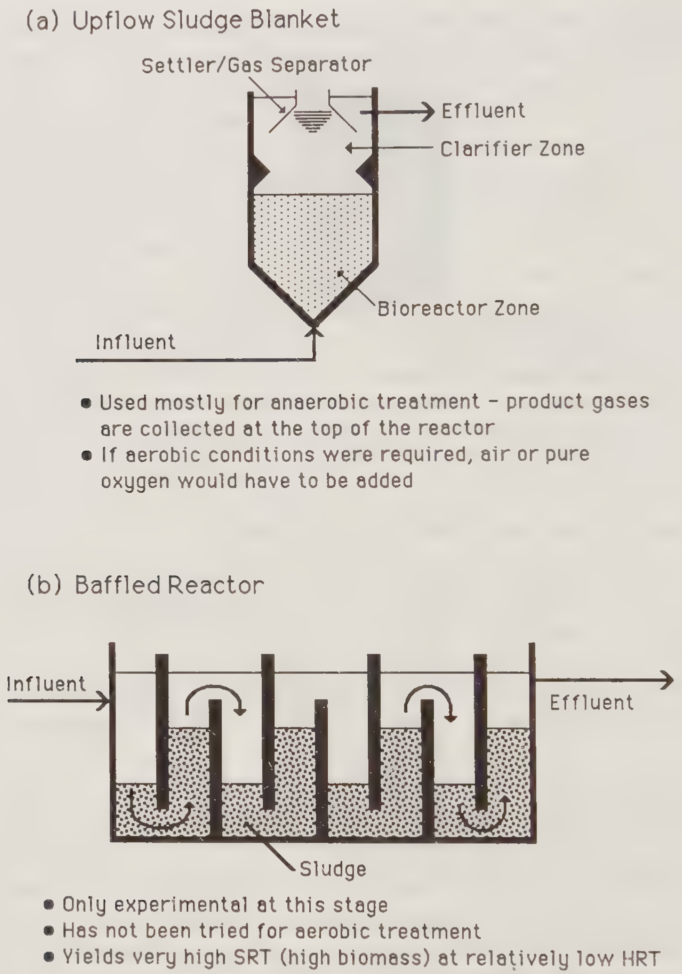

FIG. 2—*Additional AEG reactors.*

the SRT of soil bacteria may be on the order of years.) Acclimation times have been reported to vary from several weeks to several months (even up to two years for some chlorinated benzenes[3]) for the various chlorinated organics. If bacteria can acclimate to the organics contained in the contaminated water, the efficiencies shown in Table 2 might be expected from AEG and SG systems with stated operating conditions. It should be noted that with secondary utilization, 95 to 99% removal of hazardous organics may be possible in the above reactor systems.

[3]Bouwer, E. J., The John Hopkins University, personnel communication, 1985.

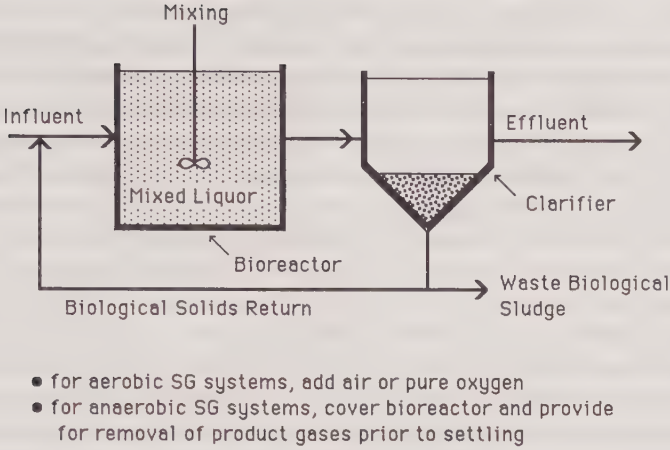

FIG. 3—*Suspended-growth system with biological solids recycle.*

TABLE 2—*Efficiencies from AEG and SG systems.*

	HRT, h	SRT, Days	Percent Removal of Hazardous Organics	Percent Removal of COD
AEG-aerobic	0.5 to 2	50 to 100	85 to 99	50 to 80
AEG-anaerobic	1 to 24	50 to 200	80 to 95	50 to 80
SG-aerobic	12 to 36	20 to 50	85 to 99	50 to 80
SG-anaerobic[a]	24 to 48	20 to 50	75 to 90	50 to 80

[a]This process is not really applicable unless high concentrations of biodegradable organics are present.

It cannot be overemphasized here that the key is acclimation time. The numbers show in Table 2 are meaningless if acclimation does not occur. Careful, patient attention to bioreclamation principles is mandatory to ensure acclimation. AEG systems have a distinct advantage in this regard.

Combination Processes—There are many possible physical and chemical processes that may be used as pretreatment before bioreclamation. For example, use of granular activated carbon (GAC), organic resins, and air stripping before biological treatment has been reported to remove substances that inhibit bioreclamation. Chemical precipitation can remove potentially toxic heavy metals. These processes may be required to ensure that biological treatment works if toxicant concentrations are too high. Whether these pretreatments are necessary can be determined with relatively simple laboratory studies. For the sake of brevity, the above combinations will not be discussed here. Only combinations that can be made to occur within the bioreactor will be considered.

During above-ground, aerobic bioreclamation, volatile contaminants will be stripped from the bioreactor. Many classes of organics and most chlorinated organics are susceptible to significant stripping during aeration. However, only a few (for example, chloroform, dichloroethylene, tetrachloroethane, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene) are reported to be stripped to any significant degree (greater than 15%) under actual treatment conditions [*21,22*]. Some removal can occur by adsorption onto the biomass, but in most cases this is thought to be a minor removal mechanism [*22*]. The majority of removal is reported to be via bioconversion. The behavior is expected and can be modeled [*36*]. It should be noted that volatile constituents can also be stripped from solution during anaerobic bioreclamation if sufficient methane is produced to act as a driving force. However, aerobic stripping is likely to be much more significant than anaerobic stripping.

Perhaps the most useful and well-tested (at least on laboratory scale) combination process is to use GAC as a medium for an AEG system (can be either aerobic or anaerobic). Such a process has been shown to work exceptionally well for treatment of phenolics and coal gasification waste waters [*23,24*]. It has also been used in Europe to treat contaminated ground and surface waters before domestic use. The advantage here is that in addition to the benefits described above for AEG bioreclamation, nondegradable organics and potentially toxic substances are removed by adsorption (it has been reported, for example, that some heavy metals can also be removed by GAC [*37*]. Biological GAC (BAC–GAC specifically seeded with bacteria and operated to enhance bacterial activity) offers an advantage over conventional GAC treatment because degradation of adsorbed organics regenerates the carbon. Thus, the need for external regeneration, which makes conventional GAC very expensive, is reduced, perhaps significantly reducing operational costs. (Note: conventional GAC is used to treat leachate generated at Love Canal. Costs of conventional GAC reported by various sources range from $10 to $60/37852 ($10 to $60/1000 gal) treated [*38*]).

The BAC system should work particularly well for contaminated waters that exhibit wide fluctuations in the nature and concentration of organics contained in the waters. The quantity and quality of contaminated ground water or leachate may change significantly from month to month (or even from day to day). The "buffer" provided by BAC for these fluctuations should lead to very stable operation.

The question as to whether to use aerobic or anaerobic conditions is a bit complex. For example, chlorinated aromatics adsorb strongly and are degraded aerobically but not anaerobically. Chlorinated aliphatics are adsorbed rather weakly and are degraded to a wider degree anaerobically than aerobically. It would seem that anaerobic BAC would offer significant potential. In this regard, it becomes important to know the nature of the biodegradable organics. Perhaps a sequence of anaerobic followed by aerobic BAC (or vice versa) may offer some significant advantages.

If GAC were to be used as the media in an AEG bioreclamation system, SRTs and HRTs would be similar to those listed above. Removal efficiences will be much higher; BAC systems would typically yield "nondetectable" for many of the priority pollutants (at Love Canal, using conventional GAC, effluent levels for priority pollutants were typically less than 20 μg/L [*38*]). The key to process feasibility and cost would be the adsorbability of the "nonhazardous" organics, which could be determined by relatively simple laboratory tests.

In-Situ Bioreclamation

Although in-situ bioreclamation of oil and gasoline spills is common, below-ground, in-situ bioreclamation of contaminated soil and ground water and leachates is not. As described earlier, the major problem is nonuniformity with respect to organic content (nature and concentration), bacterial numbers potential toxicity, nutrients, and flow. In other words, it is difficult to meet all the requirements of the "check list," especially adequate contact. If uniformity and adequate contact could be created, at least locally, in-situ bioreclamation would be feasible. The key again is providing/developing a sufficient quantity of bacteria that are acclimated to the combination of contaminants. An additional concern with in-situ bioreclamation is the rate of head-loss buildup caused by bacterial growth (hydraulic conductivity decrease). Conceptually there are three general "schemes" for in-situ bioreclamation:

(1) enhancement of existing bacteria,
(2) extraction/injection-recycle, and
(3) creation of a biologically active barrier.

Enhancement of Existing Bacteria—With this method, nutrients and perhaps an active bacterial seed would be injected via a series of wells or a shallow irrigation system into contaminated areas to enhance the growth of indigenous bacteria. The hope is that with a larger population and sufficient acclimation time, a microbial population would develop that would biotransform the contaminants at a significant rate. Reports in the literature indicate that such a technique can be successful [*39*].

With this method, a concern is the observed phenomena of downward migration of the pollutants. Perhaps the enhanced bacteria could be made (or perhaps it would naturally occur) to migrate with the pollutants, thus "cleaning up the water as they go." Whether this would actually occur is a matter of speculation at this point. The complex nature of the cracks and fissures promoting the migration of the contaminated water would in certain situations make it difficult to predict what would happen. However, this does not mean that such a process would not work; more detailed information and analysis is necessary.

Extraction/Injection-Recycle—There are many possibilities under this general heading; several have been described in the literature (Fig. 4) [*4,20,25,39*]. Both aerobic and anaerobic environments could be created by selective use of aeration (for example, pure oxygen could be injected to yield very high concentrations of dissolved oxygen that could "move" with the contaminated water, spreading over a relatively large area). The general idea would be to extract contaminated water from selected wells and combine it with necessary nutrients and acclimated bacteria (developed initially above ground and produced below ground with time) in a short-detention-time reactor (small volume), and then re-inject back in to the soil or bedrock matrix. The contaminated soil/bedrock would thus serve as an in-situ AEG reactor. As contaminants are removed from the water, it is expected that organics that had been sorbed on the soil surface would be desorbed into the passing water and removed as the treated water is recycled. In essence, this method would be somewhat analagous to land treatment of wast water. It is also analagous to the riverbank filtration method used in Europe to remove hazardous organics during drinking water treatment.

Groundwater Decontamination Systems, Inc. of Waldwickm, NJ, have developed and patented a system somewhat similar to the above-described system [*25*]. However, they advocate the use of an above-ground, SG reactor (similar to an activated-sludge system) followed by a sedimentation basin before re-injection. In addition, air is injected at selected points throughout the site to maintain aerobic conditions below ground. The process has been rea-

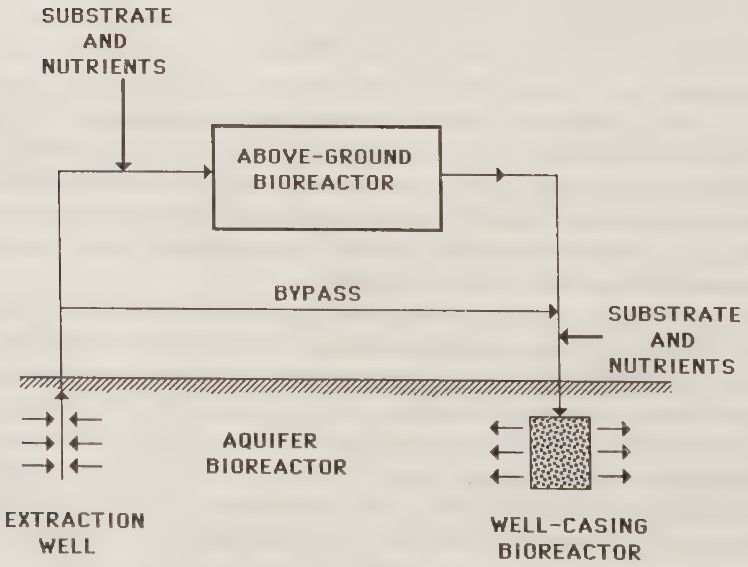

FIG. 4—*System proposed by McCarty* [4] *for bioreclamation of contaminated ground waters.*

sonably successful; the total cost is reported to be approximately \$36/3785 L (\$36/1000 gal) treated amortized over a three-year period. It would perhaps be more cost effective and, if well conceived, designed, and operated, more efficient to eliminate the activated-sludge reactor and settling tank and replace them with the mixing tank described above and allow the soil to be the only bioreactor. If it is deemed necessary to ensure that a portion of the below-ground site be aerobic; aeration could be used in the mixing basin or at selected points throughout the site.

Whether the proposed scheme is feasible depends upon the lag time required to develop the acclimated microbial population. Once the population is developed, the process will work. Water from less-polluted areas could be added for dilution if periodic toxicity is a problem. It has been shown that most toxicity is biostatic; that is, if the toxic substance is removed or diluted, the bacteria will recover [*11–13*]. Since the bacteria will be retained on the soil/bedrock matrix, none will be lost and recovery and acclimation should be possible. Removal efficiencies would seem to be limited only by the kinetics of the biological reaction. Reports in the literature suggest that under the proper conditions, it may be possible to remove some chlorinated organics down to the microgram per litre level [*2,4*].

The above discussion must be qualified with regard to the migration of pollutants. Recalling that one of the major keys for efficient bioreclamation is adequate contact between the pollutants to be removed and the bacteria that do the removing, it is imperative to keep the bacteria where the pollutants are. Whether that can be done during downward migration of pollutants is open to question.

Creation of a Biologically Active Barrier—This technique would be feasible if a majority of the contaminated ground water flows or could be made to flow uniformly in one direction. To adequately assess this alternative, detailed information concerning the general subsurface flow is required. Again, a major drawback of this approach may be the downward migration of pollutants. If the desired direction of flow was horizontal, treatment would not be very effective if a significant portion of the pollutants were moving downward. On the other hand, perhaps there is a novel way to create a biologically active barrier that would handle vertical flow.

If reasonably sure that a majority of the water could be made to flow uniformly in one direction, a biologically active barrier in the form of a "biotrench" containing acclimated bacteria and nutrients could be used to intercept and treat the contaminated water. This trench would be another form of an in-situ AEG reactor. Figure 5 is a conceptual diagram of such a system. If necessary, extraction wells or collection trenches could be used downstream to collect and recycle treated water if the degree of treatment was not sufficient. Once an acclimated population of bacteria is developed in the trench, recycle should not be necessary. In essence, ground water could be artificially forced to flow toward the "biotrench" by pumping, which may increase the operational expense.

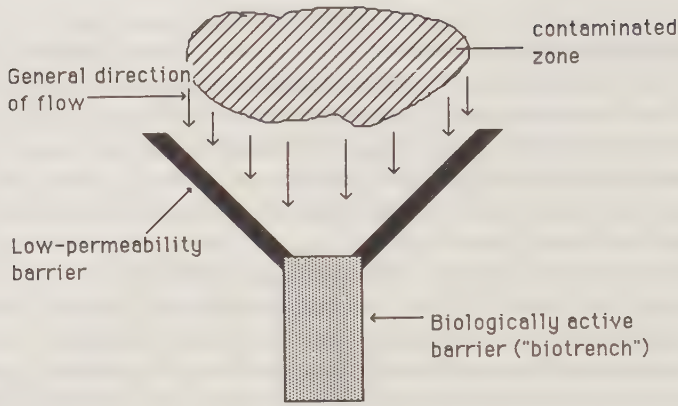

FIG. 5—*Conceptual diagram of a biologically active barrier.*

In summary, all three general in-situ bioreclamation techniques may be feasible under the right conditions. Keys include developing acclimated bacteria, determining if exogenous nutrients must be added, insuring uniform distribution of injected water or bacteria/nutrients, insuring adequate contact, controlling downward migration, and comparing projected economics with above-ground methods. Most of all, making these alternatives feasible requires patience and an understanding of the fundamentals of bacterial growth. It has been reported elsewhere that in-situ bioreclamation will work if these requirements are met [*2,34,39,40*].

Summary

The purpose of this paper was to present information showing that biological treatment of contaminated soils and ground waters and leachates is a feasible alternative to the more commonly applied remediation techniques. Efficient bioreclamation can occur when a uniform environment for the bacteria, adequate contact between the contaminated materials and the bacteria, and sufficient time to effect the degradation are provided. Maintaining the proper environment (aerobic, anaerobic, or both) includes making sure biodegradable organics are present in sufficient quantity for bacterial growth, paying attention to microbial nutrition, keeping the pH in a suitable range, and ensuring that the bacteria can adapt to the presence of toxic substances. Relatively simple laboratory tests can be performed to determine if biodegradable material is present. In some cases, small quantities of biodegradable organics may have to be added to develop a healthy population or bring about removal of low concentrations of toxic organics via secondary utilization. Proper nutrition not only includes the macronutrients, nitrogen and phosphorus, but also

micronutrients such as iron, and in the case of anaerobic environments, nickel. pH can be maintained in a favorable range with alkalinity control. Assuring minimal effects of toxic substances and acceptable bioconversion rates involves proper attention to bacterial retention time (SRT). Given sufficient time for acclimation, bacteria have been shown to degrade potentially toxic organics at relatively high rates (for example, phenol at about 2000 mg/L) and to adapt to the presence of nondegradable toxicants (for example, 250-mg/L total nickel) without a precipitous drop in organic removal rate. The means of providing adequate contact depends upon whether the treatment is accomplished above or below ground.

Selection of the bioreclamation technique to be used depends on the nature and concentration of the contaminants. With relatively high concentrations of organics, above-ground treatment is preferred. The basic choices are suspended-growth (SG) reactors (for example, activated sludge) or attached/entrapped-growth (AEG) reactors. AEG reactors have significant advantages for treating waters containing toxic and hazardous substances, the major being the provision of very high SRTs at relatively low HRTs. There are many potential options for in-situ treatment. The three basic schemes are (1) enhancement of indigenous bacteria, (2) extraction/injection-recycle, and (3) creation of a biologically active barrier. The effectiveness of each of these schemes is related to the hydraulic conductivity of the porous medium and the changes caused by bacterial growth (biomass increases as contaminants are removed and hydraulic conductivity decreases [*41*]). Combinations of above- and below-ground treatment are also possible. Patience and an appreciation for the keys to efficient biological treatment are required to made any of these options work. Economic feasibility of these alternatives also needs to be evaluated.

Finally, a word concerning the nature of the laboratory studies is warranted. These studies are critical to an objective evaluation of bioreclamation. The studies should be conducted with the understanding that an apparent lack of biodegradability can have two basic root causes: (1) the material is inherently nonbiodegradable (like lignin), or (2) there is biodegradable material there but toxic substances are preventing biodegradation. These studies need to be conducted carefully, with proper attention paid to the "check list" presented at the beginning of this paper. Such studies may take up to three to four months to adequately complete, especially when assessing anaerobic biodegradability.

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Incineration of Hazardous Waste

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Performance Assessment of Incinerators and High-Temperature Industrial Processes for Disposing of Hazardous Waste in the United States

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ABSTRACT: Since 1982, the U.S. Environmental Protection Agency (EPA) has been conducting performance assessments of hazardous waste thermal destruction facilities in the United States. The principal objective of these tests has been to characterize emissions and determine if these facilities are capable of meeting the waste destruction and control requirements of the current EPA regulations and standards. To date, the test program has involved performance assessments at 9 incinerators and over 20 high-temperature industrial processes employing hazardous waste as a fuel supplement in their operations.

The testing has typically involved stack emissions assessment for SO_x, NO_x, particulate, hydrochloric acid (HCl), carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), metals, total hydrocarbon, and quantification of specific organic compound emissions. Engineering and other process operating variables (for example, excess air, steam load, and waste to fuel ratio) have also been recorded during the test program in order to examine the potential operating bounds for these facilities.

The purpose of this paper is to summarize the extensive results of this testing program, which has, in general, indicated that high organic compound destruction and removal efficiencies (99.99%) are achievable in these facilities. Effective (99%) control of HCl emissions was attained in facilities handling chlorinated organic wastes. The current EPA particulate standard of 180-mg/dry m^3 was the most difficult standard to attain for incinerators.

KEY WORDS: hazardous waste, incinerators, industrial boilers, cement kilns, emissions sampling, trace organic compounds, thermal destruction

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The U.S. Environmental Protection Agency (EPA) has estimated that the United States generated 264 million metric tonnes (MMT) of hazardous waste in 1981 [*1*]. A significant portion of this waste was predominantly non-hazardous material (water) contaminated with hazardous materials. While only a relatively small amount of hazardous waste was managed by thermal destruction (Table 1), the Environmental Protection Agency (EPA) estimates that as much as 25 MMT could have been thermally destroyed [*2*]. It is also significant to note that more than twice as much hazardous waste was disposed in industrial processes as fuel compared to that disposed in specially designed incineration systems.

Until recently, there were only limited data available on waste destruction performance and pollutant emissions from thermal destruction devices. Studies by the EPA and others in the early to late 1970s employed a variety of evolving trace organic pollutant sampling and analysis techniques and were often targeted only towards measuring macro-destruction and combustion efficiencies [*3–5*], rather than the performance standards now required under the Resource Conservation and Recovery Act (RCRA) of 1976. Since 1981, however, the EPA has conducted a significant program of performance testing at thermal destruction facilities. The program was designed to determine the environmental impact of these operations and to provide information on the ability of these facilities to destroy hazardous waste to the degree required by the 1982 incinerator performance standards. These standards [*6*] require that facilities must demonstrate that they can attain (1) 99.99% destruction and removal efficiency (DRE) where DRE = ($[W_{in} - W_{out}]/[W_{in} \times 100]$); W_{in} = mass feed rate of the principal organic hazardous constituent [POHC] in the waste stream fed to the incinerator and W_{out} = mass emission rate of the POHC in the stack before release to the atmosphere) for each POHC in the waste feed, (2) at least 99% removal of hydrogen chloride from the exhaust gas if hydrogen chloride stack emissions are greater than 1.8 kg/h, and (3) particulate matter emissions no greater than 180 mg/standard m^3 corrected to 7% oxygen in the stack gas (correction factor = $14/[21 - Y]$ where Y = measured oxygen concentration in the stack gas on a dry basis; the measured particulate matter concentration is multiplied by the correction factor to obtain the corrected particulate matter emissions).

TABLE 1—*Hazardous waste thermal destruction facilities (1981).*

Facilities	Waste Managed, Million Metric Tonnes/Year
Incinerators (240 facilities)	1.70
Industrial boilers (~1300 facilities)	3.50
Other industrial processes (cement kilns, steel furnaces, and so forth) (~20 facilities)	0.35
Total	5.55

This paper describes the procedures and results of performance testing that the EPA has conducted over the past four years at incinerators, industrial boilers, and industrial process kilns disposing of hazardous waste. These results are being used extensively in the analysis of the environmental and economic impact of implementing existing and proposed standards for control of the operation of thermal destruction facilities.

Experimental Approach

Sampling and Analysis

The primary objective of the field testing programs was to characterize the emissions of incinerators, industrial boilers, and industrial processes burning hazardous waste under current industry operating practices in order to determine the ability of these facilities to meet existing and proposed control standards. Accomplishment of this objective required that each input and output stream be characterized to the greatest extent possible. Sampling locations, sampling and analysis methods, and quality assurance/quality control (QA/QC) planning followed established EPA guidelines [*7,8*], but were necessarily somewhat unique for each facility tested because of differences in system designs, operating practices, and waste characteristics. Typical input streams sampled included waste feed, process feed (for example, limestone feed to kilns), auxiliary or base fuel (in the case of boilers and kilns), and air pollution control system makeup and recycle flows. Output streams generally included stack gases, air pollution control device effluent (solid or liquid), bottom residues (ash), or product (cement, lime, aggregate). Where appropriate, gas samples were collected before and after air pollution control devices to characterize their contribution to performance.

Composited grab samples were employed for fuels, waste feed, ashes, residues, and product streams. Extractive sampling techniques were employed to collect integrated samples of combustion and stack gases. Semivolatile organic compounds (boiling points greater than 130°C) and particulate matter were collected using a modified EPA Method 5 (MM5) sampling train, with minor differences from site to site. Organic pollutants were extracted from all portions of the sampling train, including the XAD-2 organic sorbent, filter media, and impinger solution. Volatile organic compounds, those having boiling points $<130°C$, were generally sampled using the EPA volatile organic sampling train (VOST). However, because of the evolution of this new sampling train during the four year period of the test program, certain sites were tested with single trap systems or gas bags (EPA Method 23). Volatile compounds were thermally desorbed from the TENAX resin employed in the VOST and subsequently analyzed by GC/MS or GC/EC.

Stack and combustion gases were also typically monitored continously for oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), sulfur oxides

(SO_2), nitrogen oxides (NO_x) and, in many cases, total hydrocarbons (THC). Grab samples of wastes and fuels were also analyzed for heating value, proximate and ultimate analysis, and viscosity.

Each stream sampled was analyzed for hazardous organic constituents, chlorides, particulate or ash and, in some cases, metals of interest. Organic analysis of waste, fuel, and stack emissions samples was accomplished by GC/MS, GC/ECD, or GC/FID depending upon the selected organic groups sought in the analysis. Metals were most typically analyzed using ion capture detection methods.

Engineering and operating data were also collected for each facility. These data included waste and fuel feed rates, scrubber wastes feed, recycle and wastage rates, temperatures, and gas flow rates at critical portions of the facility and production related data for industrial processes (for example, load and steam rate for boilers and clinker production rate for kilns).

Complete descriptions of the specific sampling, analysis, and QA/QC approaches employed in the field testing are provided in EPA final reports on the test program [*9–12*].

Site Selection and Testing Rationale

Test sites were selected to evaluate waste destruction over as broad a range of facility design, operational principles, and waste characteristics as possible. This was necessary so that the EPA could generalize testing results and conclusions to the whole spectrum of hazardous waste management activities which might come under the thermal destruction regulation.

In the case of incineration, eight facilities were selected, including both commercial and on-site units. The testing encompassed rotary kiln, liquid injection, and fixed hearth technologies. Table 2 provides an overview of other important aspects of these sites.

The facility capacities ranged from 1- to 87-GJ/h heat input. Values for three key parameters, combustion temperature, residence time, and percent excess air or percent oxygen, also varied widely. Operating temperatures ranged from 650 to 1450°C and calculated residence times varied from 0.07 to 6.5 s. Excess air values fell within a range of 60 to 130%. Corresponding oxygen values in the stack gas ranged from 8 to 12%.

Waste streams with a wide range of characteristics were encountered at the eight sites (Fig. 1). Operating conditions during the tests were those selected by the plants as their normal conditions. In general, any obvious operating problems were corrected before the tests were initiated.

The industrial boiler facilities candidate test sites were screened based on representativeness of the boiler design and wastes being fired, and the availability and accessibility for cofiring tests. Within this context, preference was given to sites and waste fuels that were viewed as being less likely to attain a high level of waste destruction.

TABLE 2—*Description of incineration facilities tested.*

Facility Type	Control Device	Waste	Capacity GJ/h	Temperature, °C	Residence Time, sec
Commercial rotary kiln/liquid incinerator	packed tower adsorber ionizing wet scrubber	drummed, aqueous, liquid organic waste with carbon tetrachloride, TCE[a], perchloroethylene, toluene, phenol	87	1139	6.5
Commercial fixed hearth, two stage incinerator	electrified gravel bed filter and packed tower absorber	liquid organic and aqueous waste with chloroform, carbon tetrachloride, TCE, toluene, perchloroethylene	25	1063 Stage 1 1011 Stage 2	6.2
On-site two-stage liquid incinerator	packed tower absorber	liquid organic waste with carbon tetrachloride, dechlorobenzene, TCE, chlorobenzene, chloromethane aniline, phosgene	6	1116	5.2
Commercial fixed hearth, two stage incinerator	none	liquid organic waste with TCE, carbon tetrachloride, toluene, chlorobenzene	2	705 Stage 1 868 Stage 2	0.07
On-site liquid injection incinerator	none	liquid organic waste with aniline, diphenylamine, mono, and dinitrobenzene	4.8	681	0.20
Commercial two-stage fixed hearth incinerator	none	aqueous and organic liquid waste with carbon tetrachloride, TCE, benzene, phenol, perchloroethylene, toluene, methylethyl ketone	10	1097 Stage 1 1100 Stage 2	2.3
On-site rotary kiln with/liquid injection	venturi scrubber with cyclone separators and packed tower absorbers	liquid organic, point waste and filter cakes with methylene chloride, chloroform, benzl chloride, hexachloroethane, toluene, TCE, carbon tetrachloride	35	769 Stage 1 980 Stage 2 1450 liquid	7.3 kiln/AB 0.26 liquid
Commercial two-stage fixed hearth incinerator	venturi scrubber	aqueous and organic liquids and solid waste with methylene chloride, chloroform, carbon tetrachloride, hexachlorocylopendstadiene, toluene, benzene, TCE	75	1092 Stage 1 1045 Stage 2	3.6

[a]TCE = trichloroethylene.

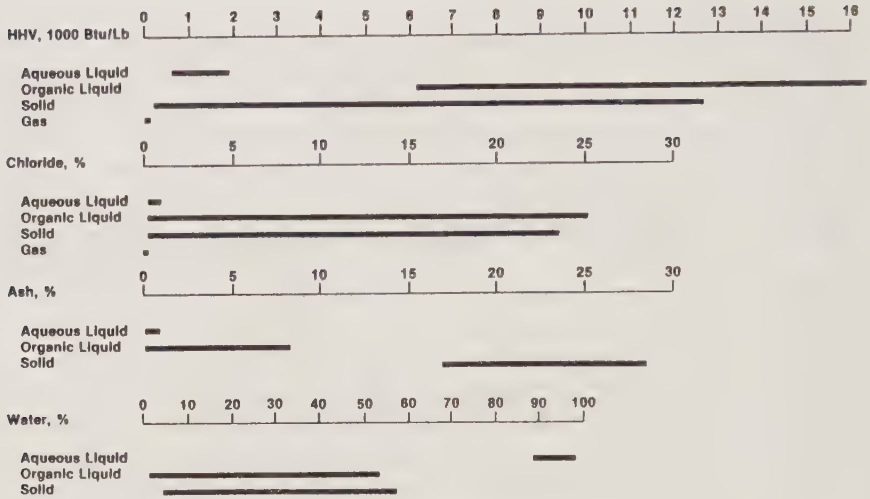

FIG. 1—*Waste characteristics.*

From a boiler design viewpoint, the test matrix addressed the major design categories of firetubes and watertubes and typical fossil fuels burned in these units. An earlier study on the estimates of time-temperature profiles in boilers had shown that although most boilers provide sufficiently high furnace temperature and residence time for efficient destruction of organic compounds, smaller units, such as firetubes and small watertubes, provide the least safety factor of time at high temperature [*13*].

Table 3 lists the eleven test sites selected for the field test program in the framework of the developed test matrix. The majority of the selected boilers were watertube designs in the 2.9- to 29-MW (10- to 100-GJ/h) size category, employing either natural gas or heavy oil as the primary fuel. The waste fuels available at the selected sites were cofired as found. However, to facilitate intrasource comparison, the majority of test boilers were cofired with a "spike" mixture of organic compounds. Spiked compounds typically were carbon tetrachloride, chlorobenzene, and trichloroethylene, which were considered difficult to destroy. This practice was also employed in the incinerator and kiln tests where carbon tetrachloride, trichloroethylene, and various freons were also employed.

The tests typically included a baseline test (primary fossil fuel only) followed by a minimum of three cofired tests for replication of results. Steady state boiler operation was sought during all testing to minimize the variation in test parameters with potential impact on DREs and other organic emissions.

Eight industrial kiln facilities were tested. Site selection here was limited to

TABLE 3—*Description of industrial boiler facilities tested.*

Facility Type	Capacity, GJ/h	Primary Fuel	Control Device	Waste
Watertube stoker	10	wood waste	multiclone	Creosote sludge with phenol pentachloropheno and napthalene
Packaged firetube	8.5	natural gas	none	alkyd wastewater with toluene
Field erected watertube	230	gas or oil	none	phenol waste
Converted stoker	90	No. 6 oil	none	methanol, toluene and chlorinated organics including perchloroethylene
Packaged watertube	110	No. 6 oil	none	methyl methacrylate by-products with carbon tetrachloride, chlorobenzene and TCE[a]
Converted watertube	60	No. 6 oil	none	paint solvents with carbon tetrachloride, TCE, toluene and chlorobenzene
Modified firetube	40	none	2 scrubbers in series	highly chlorinated organics including carbon tetrachloride
Tangentially fired watertube	250	pulverized coal	ESP	methyl acetate, carbon tetrachloride, trichloroethane chlorobenzene
Packaged watertube	62	natural gas	none	aniline waste with nitrobenzene, carbon tetrachloride, TCE, benzene, toluene
Packaged firetube	10	none	none	toluene, chlorinated organics, including carbon tetrachloride, TCE
Packaged watertube	60	No. 6 oil	none	blended waste with light oil and carbon tetrachloride, benzene, TCE, toluene

[a]TCE = trichloroethylene.

facilities actually employing hazardous waste fuels in their normal operations. As can be seen in Table 4 these included both wet- and dry-process cement kilns, a lime kiln, and three aggregate kiln facilities. The test matrix was also designed to cover a range of primary fuel type and air pollution control system design. Baseline tests (primary fuel only), and three replicate waste tests runs were employed as in the boiler evaluation program. Additionally, waste injection techniques were varied between the sites.

Discussion of Results

Tables 5, 6, and 7 summarize the waste destruction performance and emissions data collected during the test program. These data have been extracted from published and draft EPA reports on these performance tests [*7–10*].

These test results are significant in that they reveal that well operated incinerators, industrial boilers, and process kilns are capable of achieving a 99.99% DRE. All of the incinerators tested achieved this level of performance for candidate POHC compounds in concentrations greater than 1000 parts per million (ppm) in the waste feed. Candidate POHC compounds below 500 ppm frequently were not destroyed to 99.99%.

This phenomenon, which was also observed in tests of other thermal destruction devices, was unexpected. A number of possible explanations have been advanced. At the very low stack emission concentrations necessary to demonstrate 99.99% DRE for sub-500 ppm POHCs, sampling and analysis techniques may be limiting. Also at these low emission levels, a sufficient amount of POHC may actually be formed as an incomplete combustion or recombination by-product from other materials in the wastes (or fossil fuels in the case of industrial processes) to produce sub-99.99% DRE.

The EPA is conducting research to assess this concentration phenomenon. From a regulatory standpoint, however, this is not currently perceived as a problem since few if any of the low concentration compounds in the wastes identified in the EPA test program would have actually been selected as POHCs in trial burns, if existing EPA guidance on POHC selection were employed.

Industrial boilers, particularly the larger water tube units, are acceptable devices for waste destruction. Cement kilns, lime kilns, and lightweight aggregate kilns with adequate combustion control and waste atomization all met or exceeded the 99.99% DRE. It is also important to note that in all cases the destruction and removal efficiencies observed were due to destruction rather than removal or capture of hazardous organics. Ash, scrubber water, and air pollution control device residues were typically below detection limits for POHCs and organics.

All incinerators and industrial process kilns tested met or approached the RCRA HCl removal standard. Industrial boilers typically have no existing controls for HCl, but none exceeded the 4-lb/h emission standard since wastes with low net chlorine content were employed.

TABLE 4—*Description of industrial kiln facilities tested.*

Facility	Capacity GJ/h	Primary Fuel	Control Device	Waste
Wet process cement kiln (non-atomized waste)	140	No. 6 oil	fabric filter	waste liquids including, methylene chloride, chloroform, carbon tetrachloride
Wet process cement kiln (atomized waste)	170	coal	ESP	waste liquids, including methylene chloride, MEK[a], trichloroethane, toluene, Freon 113
Dry process cement kiln (non-atomized waste)	228	coal/coke	ESP	waste liquids, including methylene chloride, Freon 113, MEK, toluene, trichloroethane
Dry process cement kiln (atomized waste)	300	coal/coke	fabric filter	waste liquids, including trichloroethane, trimethylbenzene, xylene, methylene chloride
Lime kiln (atomized waste)	50	coke/natural gas	fabric filter	waste liquids, including methylene chloride, MEK, trichloroethylene
Shale aggregate kiln (atomized waste)	35	coal	scrubber	waste liquids, including perchloroethylene, methyethyl
Clay aggregate kiln	20	coal	scrubbers	waste liquids, including methylethyl ketone, perchloroethylene and toluene
Clay products kiln (atomized waste)	37.5	waste oil	fabric filter	waste liquids, waste oil, Freon 113, perchloroethylene carbon tetrachloride, benzene toluene, trichloroethylene

[a]MEK = methylethyl ketone.

TABLE 5—*Incinerator performance and stack emissions data (reported as averages for each site).*

Facility Type	O_2, %	CO, ppm	THC, ppm	DRE[a], (Number of Nines), %	Particulate, mg/m^3	HSI Control, %
Commercial rotary kiln/ liquid incinerator	10.5	7.9	<1.0	99.9993	1508	99.4
Commercial fixed hearth, two stage incinerator	11.4	6.9	1.0	99.994	400	98.3
On-site two-stage liquid incinerator	8.3	10.5	6.4	99.994	61	99.7
Commercial fixed hearth, two-stage incinerator	11	14.8	1.4	99.997	200	[b]
On-site liquid injection	12.1	13.0	<1.0	99.99997	207	[b]
Commercial two-stage	9.9	1.4	<1.0	99.998	900	[b]
On-site rotary kiln	9.7	544	61.7	99.9993	23	99.9
Commercial two-stage fixed hearth incinerator	13.6	2.6	1.6	99.996	169	98.3

[a]Mass weighted overage for all POHCs >100 ppm in waste.

[b]This facility did not employ a control device for HCl. However, HCl emissions were less than the 1.8-kg/h emission standard because of low chlorine content in the waste feed stream.

TABLE 6—*Summary of boiler performance.*

Facility Type	Load, %	O_2, %	Residence Time, s	Average Volumetric Heat Release Rate, KW//m³	DRE[a]	W/F[b], %	NO_X[c], ppm	CO[c], ppm
Watertube stoker	100	6 to 16	1.2	509	99.98	40	163 to 210	900 to 1200
Packaged firetube	25	4 to 6	0.8	739	99.991	0.1 to 0.5	40 to 65	47 to 88
Field erected watertube	26	10	2	78	99.9996	37	61 to 96	18 to 21
Converted stoker	78	4 to 6	1.1	339	99.998	18 to 48	193 to 250	75 to 127
Packaged watertube	36 to 73	6 to 7	1.1 to 0.5	960	99.995	19 to 56	164 to 492	83 to 138
Converted watertube	53	7 to 11	2	107	99.98	8.7 to 10.1	243 to 328	109 to 139
Modified firetube	44	8	0.4	807	99.998	100	67 to 74	146 to 170
Tangentially fired watertube	100	6	2	180	99.991	2.4 to 4.3	393 to 466	142 to 201
Packaged watertube	65	2	1.8	343	99.998	8.2	64 to 78	
							410 to 1125[d]	46 to 750
Packaged firetube	50 to 100	3 to 8	0.7 to 0.3	1240	99.999	100	85 to 203	20 to 135
Packaged watertube	82	4	1.8	269	99.9997	49	154 to 278	102 to 119

[a]Mass weighted average for all POHCs in the waste >100 ppm.
[b]W/F = waste heat input as a percent of total heat input.
[c]Range of average values across individual sites and runs including baseline.
[d]Higher values are for high nitrogen waste firing.

TABLE 7—*Summary of industrial kiln performance.*

Facility Type	Test[a]	DRE[b] (No. Nines)	Particulates, kg/MG	HCl, kg/h	NO_x, ppm	So_2, ppm	*W/F*, %[c]
Wet process cement kiln	W	2.2	0.27	0.36	68	450	25
(nonatomized waste)	B	...	0.26	0.09	136	279	...
Wet process cement kiln	W	4.6	0.27	2.1	478	265	15
(atomized waste)	B	...	0.26	0.6	371	636	...
Dry process cement kiln	W	4.8	...	11.5	814	19	45
(nonatomized waste)	B	...	...	1.3	620	7	...
Dry process cement kiln	W	4.2	...	0.47	486	27	15
(atomized waste)	B	...	...	0.25	680	27	...
Lime kiln (atomized waste)	W	4.7	0.11	0.20	446	596	30
	B	...	0.10	0.09	386	553	...
Shale aggregate kiln (atomized waste)	W	>4.0	0.33	2.1	...	...	100
Clay aggregate kiln (atomized waste)	W	4.8	0.58	0.023	162	1130	59
Clay products kiln (atomized waste)	W	>4.0	0.002	0.84	...	...	100

[a]W = waste testing and B = baseline (no waste firing).
[b]DRE = destruction and removal efficiency (for example, 4.5 nines = 99.995%).
[c]Percent of total heat input provided by waste fuel.

Compliance with the particulate standard of 180 mg/Nm^3 was not achieved at half of the incinerators tested. Particulate control devices were operated at five of the eight facilities, and two of these five failed to achieve the standard. Two of the three facilities without control devices also failed the particulate standard. Data from this study suggest that any facility firing wastes with ash content greater than 0.5% will need a particulate control device to meet the standard.

No significant changes in particulate emissions were observed for industrial boilers and certain of the industrial process kilns when they fired waste fuels. Some increased emissions have been observed in kilns employing electrostatic precipitators (ESP) for particulate control. These increases were attributed to changes in the electrical resistivity of the particles caused by the presence of increased chloride levels. Adjustments in ESP operation or controlling chlorine input could correct this in most cases.

Analysis of the data from the incinerator test program revealed that there was no absolute level of mean combustion temperature, mean gas phase residence time, or carbon monoxide emission concentration, which correlated with achieving 99.99% DRE. It appears at this time that any parametric relationships between DRE and these parameters are in all likelihood facility specific and that waste characteristics, waste atomization, and combustion chamber mixing likely play an equally important role in achieving high DRE. Analysis did reveal, however, that CO and total hydrocarbon (THC) emissions may provide indication of changes in incinerator performance and gross malfunctions in the combustion process. Similar observations of this were apparent in the boiler emission test results.

Data from the industrial boiler testing indicated that a relationship existed between NO_x formation (through thermal NO), furnace volumetric heat release rates, and DRE. Higher NO_x emissions and higher volumetric heat release rates generally corresponded with higher measured DREs. DREs less than 99.99% were found to generally correspond to NO_x gas concentrations of less than 250 ppm and volumetric heat release rates less than 500 kW/M^3. The higher the NO_x and volumetric heat release rates, the higher the range in measured POHC DRE. These trends are felt to indicate that lower boiler loads may be more likely to result in lower DREs and that the temperature dependence of POHC destruction is more significant than furnace residence time. This conclusion is not meant to indicate a definite relationship but rather a potential trend that warrants further investigation.

In the case of industrial kilns, NO_x emissions were not significantly affected by waste combustion. NO_x concentrations vary over time at the same kiln and are affected by oxygen input, primary to secondary air ratio, and temperatures. Sulfur dioxide (SO_2) emissions, however, generally decreased when waste fuel was used to replace a sulfur-containing fossil fuel; SO_2 emissions were found to be a function of several variables, such as sulfur loading, oxygen input, and temperatures. Cement kilns can be operated to obtain low SO_2

concentrations. Lime kilns are operated at higher SO_2 levels deliberately to avoid sulfur in the lime product.

The current RCRA standards regulate destruction and removal only for the major hazardous compounds in the waste. Under poor combustion conditions, many compounds may only partially decompose and form products of incomplete combustion (PICs), which are also hazardous compounds of concern if emitted. For the purpose of the EPA test program, compounds were considered to be PICs if they were regulated organic compounds (that is, listed in Appendix VIII of CFR 40 Part 261), which were detected in stack emissions, but not present in the waste feed at concentrations greater than 100 ppm. Table 8 summarizes the PICs most frequently identified in the EPA testing of incinerators and industrial boilers. At this writing, detailed PIC analyses have been completed for only three cement kiln tests. The most common PICs identified during these tests were benzene, benzaldehyde, toluene, and various naphthalenes.

For incinerators the total mass emission of PIC compounds was typically equal to or less than the emissions of POHC. Data from the tests suggest that benzene, toluene, chloroform, tetrachloroethylene, and naphthalene have a high potential for appearing as by-products of the combustion of organic wastes.

TABLE 8—*PICs most frequently detected in stack emissions.*

PIC	Number of Facilities	Concentration, ng/L
Incinerators		
benzene	6	12 to 670
chloroform	5	1 to 1330
bromodichloromethane	4	3 to 32
dibromochloromethane	4	1 to 12
naphthalene	3	5 to 100
bromoform	3	0.2 to 24
chlorobenzene	3	1 to 10
tetrachloroethylene	3	0.1 to 2.5
1,1,1-trichloroethane	3	0.1 to 1.5
toluene	2	2 to 75
o-nitrophenol	2	25 to 50
methylene chloride	2	2 to 27
phenol	2	4 to 22
Boilers		
chloroform	5	4.2 to 1900
tetrachloroethylene	5	0.3 to 760
chloromethane	4	4.6 to 410
methylene chloride	4	83 to 2000
benzene	3	9.4 to 270
1,1,1-trichloroethane	3	5.9 to 270
1,2-dichloroethane	3	1.3 to 1200
1,1-dichloroethylene	2	0.21 to 38
1,1,2,2-tetrachloroethane	2	4.6 to 16
toluene	2	46 to 960

For industrial boilers total PIC mass emissions were about one order of magnitude or greater than mass emissions of POHC. Chloromethane, methylene chloride, and chloroform accounted for more than 75% of the total chlorinated PICs. Toluene contributed the bulk of total nonchlorinated PICs.

The EPA is conducting continuing research to assess the nature and magnitude of PIC emissions from hazardous waste thermal destruction. Current data suggest that for thermal destruction facilities, which are achieving good POHC DRE, and PIC emissions, are not of environmental concern. Consequently, the EPA does not currently have plans to regulate PICs under RCRA. The EPA's research program is striving to assure that potential PIC problems do not exist for wastes not yet tested or for marginal thermal destruction conditions (for example, DRE failure conditions). Understanding the mechanisms for PIC formation and for PIC control through optimization of combustion conditions is therefore quite important.

Conclusion

Thermal destruction is an effective and broadly applicable technique for destruction of organic hazardous waste. Performance tests conducted by the EPA have indicated that incinerators and many high-temperature industrial processes are capable of achieving existing performance and emissions standards.

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Liner Assessments

Robert M. Koerner[1]

Use of Flexible Membrane Liners for Industrial and Hazardous Waste Disposal

REFERENCE: Koerner, R. M., **"Use of Flexible Membrane Liners for Industrial and Hazardous Waste Disposal,"** *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 195–207.

ABSTRACT: This paper presents an overview of synthetic liners, called flexible membrane liners (FMLs), as used in the containment of solid wastes and their leachates in landfills. Details of FML manufacturing and properties are presented. This is followed by methods to evaluate chemical compatibility, elements of FML design, and various construction details. A series of topics for further research and development concludes the paper.

KEY WORDS: cap (structures), closures, hazardous waste, wastes, landfills, linings, membranes, seams (joints), slopes, flexible membrane liners, geomembranes, landfill caps, landfill closure, landfill liners, pond liners, seam inspection, seam testing, secure landfills, slope stability, solid waste, thermoplastic, thermoset

The general classifications of solid waste materials can be grouped into municipal, industrial (or residual), hazardous, and radioactive categories. Within these categories, municipal and industrial wastes are by far the most voluminous, while hazardous and radioactive wastes are by far the most dangerous. Unfortunately, many people are not aware of these distinctions or have tended to avoid such classifications and treat all solid waste as a single entity. The impact of such a viewpoint is that the entire solid waste field is undergoing extreme pressures to create landfills for enormous quantities of extremely heterogeneous materials. This, in turn, requires the utmost care in all aspects of design, construction, inspection, and monitoring.

The main line of defense in any landfill (certainly for hazardous and radio-

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active solid wastes) is the liner placed beneath the landfill and on the side slopes. As outlined by Kays [*1*], such liners can be grouped into rigid (concrete or asphalt paved), flexible from natural materials (typically clay soils in the montmorillonite family), and flexible from synthetic materials. Of the two types commonly used, clay and synthetic liners are by far the most common. Both types have advantages and disadvantages that are beyond the scope of this paper to elaborate upon. Suffice it to say that both types should see continued use and often in conjunction with one another. This paper will concentrate entirely on flexible liners made from synthetic (or polymeric) materials. They are also called pond liners, flexible membrane liners, and geomembranes. The term flexible membrane liner (FML) will be used here.

Overview of Flexible Membrane Liners (FMLs)

The history of FMLs began with the vulcanization of rubber during World War II and the use of butyl lined ponds in the late 1940s and 1950s. The use of polyvinyl chloride (PVC) liners followed in the 1960s, with subsequent numbers of polyethylene (PE) varieties increasing in the 1970s. This trend is continuing with the most recently developed system, high-density polyethylene (HDPE), being introduced for liners in about 1980.

The production of FMLs for use as liners follows a number of carefully detailed stages. Each is often performed by a different organization, which can lead to a certain amount of difficulty in determining responsibility if problems arise.

First, a chemical company (or companies) supplies the raw material product(s). Second, compounders blend the raw materials and make additions to a specific formulation. The mix is heated, sent through a vacuum extruder, and forced between rollers to form a sheet varying in width from 1.2 to 8.0 m and in thickness from 0.01 to 0.25 cm. Third, fabricators, often a separate company, take the sheet with a specific project (that is, an order) in mind and form a field-ready product. Individual sheets are sometimes laminated and calendered with an open weave fabric placed between them. This fabric, referred to as a scrim reinforcement (or simply reinforcement) makes the FML more resistant to impact, puncture, tear propagation, and dimensionally stabilizes it but does little to reinforce the soil subgrade beneath the lining. The fabric is usually nylon, polyester, or polypropylene. Fabricators then factory-seam sheets together for shipment to the job site. In certain instances they can completely fabricate small liners. This includes openings for pipes and other appurtenances, corners for edges, and various other details as required. Liners 0.5 mm (20 mils) or less in thickness can sometimes be accordian-pleated and shipped in boxes. More often, however, they are rolled on spools and covered for protection against damage and ultraviolet light degradation during shipment to the job site. Fourth, installation contractors (sometimes the same organization as the fabricators) are the final group involved as they bid

on the project and, if successful, do the buying and installation. They follow plans and specifications prepared by the designer and work directly for the inspection team and owner or both.

Of course, there are many variations of the above sequence of operations, for example, some polyethylene is produced and often installed by a single organization. The above sequence of manufacturing events has led to a wide variety of different types of FMLs. Table 1 gives a listing of those most often used for landfill liners.

Concerning the properties of FMLs, much has been written and yet still much remains to be done. There are many organizations working on test methods and standards. In general, they characterize the tests as follows:

- physical properties
- mechanical properties
- chemical durability
- thermal stability
- biological stability

Table 2 gives the usual range of values of some properties within each category. To be noted is that chemical compatibility must be specifically evaluated. While this is not too burdensome when the composition of the contained material is known, for example, in a reservoir situation, it is extremely troublesome for landfills. This is due entirely to the complex nature of the leachate formed during the lifetime of the landfill. Numerous references are available discussing the subject of leachate quality [*2,3*]. It is indeed extremely heterogeneous and often contains pollutants that are at the extreme

TABLE 1—*Major types of FMLs in current use.*

Plastics
polyvinylchloride (PVC)
polyethylene (LDPE, MDPE, HDPE, referring to low, medium and high density)
chlorinated polyethylene (CPE)
polyamide (PA)
Rubbers
isoprene—isobutylene (butyl)
epichlorohydrin rubber
ethylene propylene diene monomer (EPDM)
polychloroprene (neoprene)
ethylene propylene terpolymer (EPT)
ethylene vinylacetate (EVA)
Combinations
PVC—nitrile rubber
PE—EPDM
PVC—ethyl vinyl acetate
cross-linked CPE
chlorosulfonated polyethylene (CSPE)

TABLE 2—*FML properties and typical ranges.*

Property	Ranges
Physical	
thickness	0.03 to 0.23 cm or 10 to 90 mils
specific gravity	0.85 to 1.05
weight	700 to 3500 g/m^2
Mechanical	
tensile strength at yield	
unreinforced	1 to 5 kg/cm width
reinforced	5 to 20 kg/cm width
tensile strength at break	
unreinforced	1 to 5 kg/cm width
reinforced	20 to 60 kg/cm width
elongation at yield	
unreinforced	20 to 100%
reinforced	10 to 30%
elongation at break	
unreinforced	100 to 500%
reinforced	70 to 250%
Modulus of elasticity	
unreinforced	10 to 350 MPa
reinforced	400 to 2000 MPa
tear resistance	
unreinforced	1 to 10 kg
reinforced	10 to 40 kg
Impact Resistance	
unreinforced	0.05 to 2 kg·m
reinforced	4 to 40 kg·m
soil to liner friction	50 to 100% of soil friction
seam strength (shear and peel)	50 to 100% of liner strength
Chemical	
volatile loss	can begin 1 to 20 years after compounding
ozone resistance	varies with liner and location
ultraviolet light resistance	varies with liner and location
chemical compatibility	must be specifically evaluated
Thermal	
hot climates or conditions	usually no problem regarding material
cold climates or conditions	decreases in ductility, difficult to seam
Biological	
stability to microbe attack	usually no problem
burial resistance	generally good

of hazardous or radioactive limits or both. In such cases, chemical compatibility is at the heart of FML selection.

Chemical Compatibility

Considering that the design lifetime of a landfill varies from 20 to 40 years, the question must be posed as to the liner's compatibility with the contained leachate over this time frame. While field performance data could give excel-

lent insight, FMLs are much too recent for such an approach. The oldest FML lined hazardous landfills are approximately ten years old at the present time. Experience has told us, however, that when a chemical or leachate is reactive with a FML, it generally evidences itself within days or weeks. Using this as a reference point, most designers and agencies utilize an incubation process of the FML in the liquid to be contained, and periodically sample and test the exposed FML. If changes in the property being tested are observed the suggestion is that an interaction is ongoing and thus the candidate FML is unacceptable. If no changes are found it is acceptable. Thus complete inertness of the FML to the exposure is demanded.

The incubation process referred to previously can take three forms:

- immersion
- tubs
- pouch

In the immersion method the FMLs are suspended lengthwise in the leachate exposing both sides and the edges. While this is the customary method for incubation it does not realistically simulate the in-situ behavior of the FML. The tub method uses a dishpan size tub in a suitable frame and places the FML in the tub, then the leachate in it (Fig. 1). It is felt by the author that it reasonably simulates in-situ performance. The pouch method uses the FML to form a pouch, or pillow, with the leachate contained within. In so doing, seams are required; thus both the FML and its seams are being evaluated.

Whatever the incubation method, the FMLs are systematically removed after gradually increasing time periods and tested. An incubation time series of 5, 10, 15, 30, 60, and 90 days exposure is often used. Results are then compared to results from the as-received material. While these tests are usually performed at room temperature, some manufacturers recommend the use of elevated incubation temperatures, for example, 70°C (158°F). However, no known relationships between time and temperature (versus FML degradation) are known to exist.

The method of testing is the next decision to make. Usually some form of physical or mechanical test or both is used. Figure 2 shows such results with time, where weight change increased, as did failure load and modulus, but failure strain decreased. Clearly a reaction with the acetone was occurring in which the FML became more brittle, obviously an unacceptable situation. By point of reference, manufacturers often require physical properties to change less than 3% and mechanical properties to changes less than 10% for an acceptable situation.

An alternative testing procedure is by measuring transmission or diffusion properties [*4,5*]. Here one could evaluate water vapor transmission, radioactive tracer transmission, and water or vapor diffusion. Changes as a function of incubation time are again the focus, with results being plotted in a similar manner as shown in Fig. 2 [*5*] for such data.

FIG. 1—*Photographs of tub incubation of FMLs to various chemicals or leachates or both.*

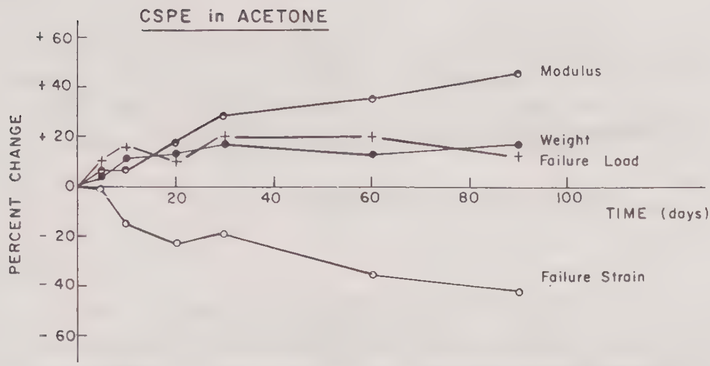

FIG. 2—*Physical and mechanical property response to incubated FML in acetone.*

Elements of Design

Once the liner material has been decided upon, a number of design steps must be addressed. Most are reasonably straightforward, and rational design methods are available or currently emerging [*6*].

Geometric Considerations

Based on the estimated quantity of waste to be landfilled and the topography of the actual site, relationships of area to total fill height can be generated. From here the depth beneath the ground surface (consistent with the soil stratification and water table) and the eventual upper elevation can be determined.

Cross Sections

Landfill cross sections always contain a leachate collection system above the liner, but from here the similarity ends. Figure 3 shows a few of the many possibilities that are available. The single liner system can generally be used for municipal or industrial wastes, but the double liner systems are generally required for hazardous and low-level radioactive wastes. The double liner system with at least 90-cm (36-in.) clay backup is the current recommendation of the U.S. Environmental Protection Agency (EPA) for hazardous material landfill liners.

The sketches of Fig. 3 do not convey the difficulty that these sections are to construct. Not only is the actual placement of the liners, drainage stone, and geotextiles difficult, the site grading and compaction are extremely demanding. Both leachate collection and leak detection systems are gravity drained at slopes often as low as 2%. Yet they must drain to outlet wells outside of the

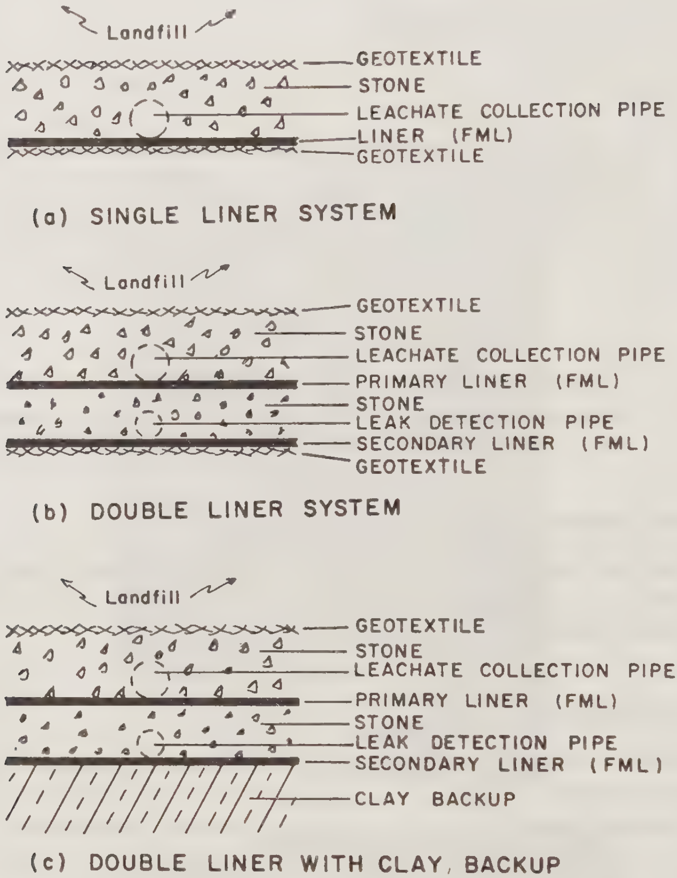

FIG. 3—*Cross sections of landfill liner systems.*

lined containment area itself. It is very difficult construction work requiring continuous on-site inspection.

FML Thickness

Theoretically, the thickness of a liner on a firm nonyielding subsoil without any bending or torsional stresses can be negligibly thin. Only when differential movements occur does thickness play a part. In such cases of pipe breaks or localized subsidence, designs for thickness based on accepted methods of statics can be formulated. In performing these designs, thickness of 0.50 mm (20 mils) or greater usually result [6]. Note that EPA minimum thickness is 0.75 mm (30 mils).

Side Slopes

The proper design of stable side slopes falls within the realm of geotechnical engineering. Numerous approaches are available, which can be either approximate or exact [*3*]. Often, soil side slopes are designed as steep as 26°, which is 2 (horizontal) to 1 (vertical), but other considerations often dictate lower slope angles.

Cover Soil

For a number of reasons, FMLs should have a cover soil placed above them. These include protection against ozone and ultraviolet light degradation, puncture, impact, and vandalism. There are a few disadvantages, however, and these are difficulty in leak detection and repair, and stability of the cover soil on the liner at the side slopes. Geotechnical engineering design methods are available for proper cover soil design. It is usually seen that because of the low frictional resistance of the cover soil to the liner (typically 50 to 90% of the soil's friction), the side slopes must be lower than that dictated by their own stability. In other words, cover soil stability usually dominates over in-situ slope stability. With tapered thickness cover soil designs, the slope angle often decreases to 18° (3 to 1), and with uniform thickness cover soil, designs down to 14° (4 to 1) often result. Careful consideration must be given to this particular detail.

Runout Length and Anchor Trench

As the liner extends up the side slopes it eventually reaches the ground surface where it extends horizontally and then drops into a shallow anchor trench. Designs are available that consider this aspect of the liner and result in design charts as shown in Fig. 4. For example, by assuming a 61-cm (24-in.) runout length and a factor of safety of 2.0 the anchor trench must be approximately 25-cm (10-in.) deep for the conditions stated. Other combinations can be developed as need be.

Caps and Closures

Once the landfill is completed it must be capped or closed to prevent infiltration of water and safety against accidental excavation or penetration. Such caps are usually 0.6 to 1.2 m (2 to 4 ft) thick and are well suited for construction with clay soils. This is usually the case. In the absence of the clay soil, however, FMLs can be used, and Fig. 5 shows some possible cross sections. The double closure system has been used for an in-situ stabilized sludge lagoon where the possibility of differential settlements was quite high. Thus a high-strength geotextile was used immediately above the stabilized landfill to

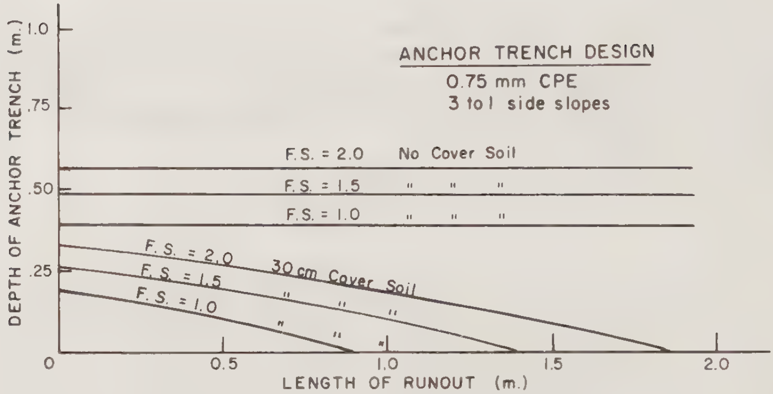

FIG. 4—*Design curves for anchor trench depth versus runout length at various factors of safety for conditions stated, after Koerner* [6].

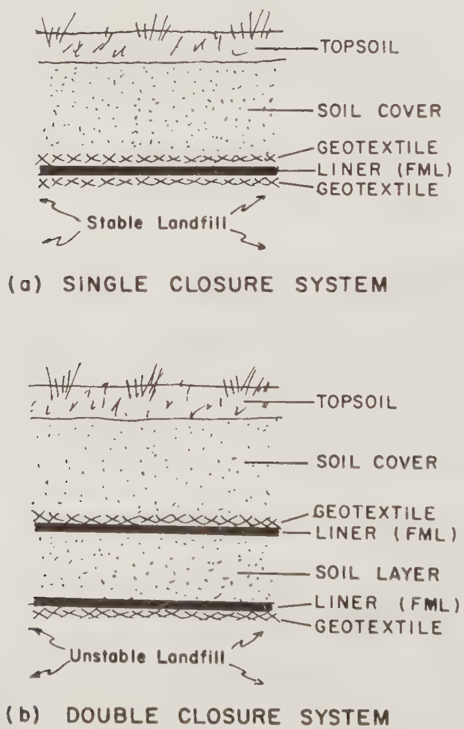

FIG. 5—*Cross sections of landfill closure (caps) systems.*

even out the anticipated settlements and make a working platform for the rest of the capping system.

Construction Details

More than in any other construction activity (perhaps on an equal footing with nuclear construction) is hazardous landfill liner construction dependent upon quality assurance and quality control. It is absolutely essential to construct 100% of the liner properly, and this includes all seams and connections. FML manufacturers have excellent information in this regard so only a few salient points will be discussed.

Seams

The general philosophy of seams is to minimize the amount of field seaming by creating the largest panels that can be reasonably handled. This in turn necessitates greater amounts of factory seams, which are generally of higher quality than field seams.

Various FML materials are seamed by different methods. Table 3 gives some insight into their variety and a qualitative feeling of which aspect of the method has greatest importance. A considerable effort in this area has been expended by FML manufacturers, and their literature should be consulted once the FML has been selected. It should be noted, however, that when seams are made from a dissimilar material than the FML itself, compatibility with the leachate must be addressed. In this regard, the pouch method referred to earlier has a great deal of merit.

TABLE 3—*FML seaming methods including major features and concerns.*

Method	Pressure	Heat	Location	Concerns[a]
Adhesive (liquid)	yes	no	field	W, C
Adhesive (tape)	yes	no	field	W, C
Solvent	yes	no	field	W, D
Solvent (bodied)	yes	no	field	W, D, T
Vulcanization	yes	yes	field	D, I
Dielectric	yes	yes	factory	D, T
Heat	yes	yes	field	D, T
Welding	yes	yes	field	D, T
Welding (agitated)	yes	yes	field	D, T

[a] W = workmanship. C = compatibility. D = duration (time). T = temperature. I = current.

Connections and Appurtenances

At every location where a pipe, well, drain, support column, or other interruption of the planar lining is necessary, a seam must be made. These are difficult details to make and are often the cause of leaks. Again, manufacturers' literature should be consulted for details for most of the common situations.

Seam Inspection

A crucial aspect of FML construction is seam inspection, particularly that of field seams. They must be 100% inspected. An overview paper by Frobel [7] gives excellent insight into the various methods, which include the following:

- mechanical point method
- air lance method
- vacuum box test
- double seam inflatable test
- electric sparking
- ultrasonic tests

Each technique has its own advantages and disadvantages. While not fully developed the ultrasonic method holds the promise of a rapid, high-quality test, which gives immediate feedback of the test results.

Leak Location Methods

Once a leak through the liner (primary liner if it is a double liner) is observed, its location becomes of paramount importance. A number of attempts have been made at solving this problem, they include:

- gradients drawn from downstream monitoring wells
- electrical resistivity surveys
- acoustic emission monitoring
- time domain reflectrometry monitoring
- electric current propagation

Unfortunately, none of the above will define the location of a liner leak within the landfill itself at a reasonable cost or accuracy or both. This area is certainly one that requires a concentrated research and development effort.

Summary and Conclusions

Flexible membrane liners (FMLs) are currently being used with all hazardous and low-level radioactive landfill wastes and often appear as doubly lined systems. It seems to be an obvious extention that industrial and municipal

landfills will soon be lined in a similar manner. This paper has presented an overview of the FML industry (as pertains to landfill liners) and then proceeded to enter into the discussion of three major topics, that is, chemical compatibility, elements of design, and construction details.

Although when using such approaches as were described one can currently "build with confidence," there still remains some questions and uncertainties. Some of these areas of concern, which should be addressed as soon as possible, are as follows:

- Development of test methods simulating in-service behavior of the FML (durability and ageing tests)
- Development of test methods and standards for FMLs
- Procedures for synthesizing landfill leachates
- Test procedures for predicting chemical compatibility, including accelerated ageing tests
- Automated field seaming methods
- More reliable and easier to use field seam test methods
- Development of leak location methods

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Migration of Leachate Solution Through Clay Liner and Substrate

REFERENCE: Yong, R. N., Warith, M. A., and Boonsinsuk, P., **"Migration of Leachate Solution Through Clay Liner and Substrate,"** *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 208–225.

ABSTRACT: The migration of various contaminants in a sensitive soil, used as liner and in-situ substrate in an actual landfill site, is investigated in controlled laboratory column leaching tests. Using the actual leachate collected from the site, the laboratory tests show good attenuation of the heavy metals studied and lesser attenuation of the salts. Comparison between predicted and concentration profiles, using Cl as an example, shows that there is significant need to account for the time and spatial variation of the specific dispersion coefficients – caused by continued leaching or intrusion of the contaminants – if proper accord between predicted and measured profiles is to be achieved.

KEY WORDS: migration, contaminants, leaching, leachate, sensitive clay, heavy metals, dispersion coefficient, buffering capacity

Improper or inadequate site preparation and management of disposal of solid municipal and industrial waste can lead to problems associated with contamination of the local subsurface environment and ground water. Because the leachate solution produced from such wastes can be composed of a highly complex mixture of soluble organic, inorganic, ionic, nonionic constituents, together with microorganisms, their interaction with the clays that comprise the containment basin and substrate will result in (1) successful containment of the offending leachate solution via attenuating and sealing characteristics of the clay material, (2) controlled migration of the various constituents through reliance on the buffering capability of the soil materials, and (3) undesirable contamination of the local subsoil and ground water

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through uncontrolled and relatively unattenuated migration of offensive constituents.

Changes in the composition and concentration of leachate migrating from waste containment ponds and sanitary landfills for industrial and domestic wastes result from the occurrence of one or more of several processes, for example,

(1) diffusive or dispersive mass transport of contaminants through the soil system or both,
(2) interactions and reactions that occur within the soil system,
(3) adsorption of contaminants onto surfaces of soil constituents,
(4) ion-exchange,
(5) microbial interaction and activity leading to biodegradation and generation of various products, and
(6) precipitation.

Depending on the nature and composition of the contaminant, these processes may be of varying importance and significance in consideration of leachate migration through clay soils, used either as liner material or containment substrate or both.

In this study, the use of a natural (in-situ) clay as an expedient economic liner material has led to questions as to the capability of the in-situ compacted clay to function as a liner. The actual working landfill site being studied, which is located near Montreal, began operations in early 1981. At this site, the natural sensitive clay in the excavated site was compacted and used as "lining" material. Compaction in-place by rollers was designed to achieve 100% standard Proctor density. Figure 1 shows the general landfill scheme used in containment of the solid (municipal) waste material. In Feb. 1984, ten

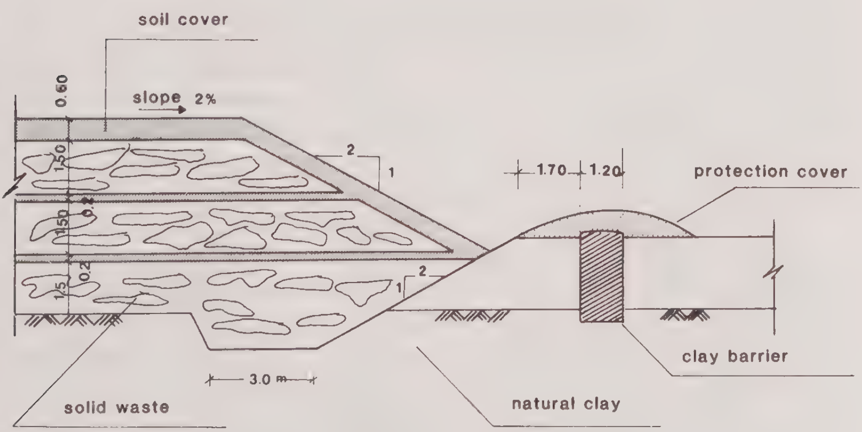

FIG. 1—*General landfill scheme used in actual landfill state.*

sampling points (monitoring wells) were installed for monitoring the early migration of contaminants into the subsurface environment. Each monitoring well was 0.1 m in diameter and 4 m in depth. This allowed the bottom of the wells to penetrate about 1 m into the clay substrate. Of the three wells located inside the clay barrier, one was located directly in the fill itself, and the remaining two on the periphery of the fill. The remaining seven wells were located just outside the clay barrier at various locations surrounding the fill. At a later time, additional monitoring wells will be installed to study contaminant migration at greater depths of the clay stratum.

Because of the need to define or characterize the effectiveness of the natural sensitive clay in control of migration of contaminants obtained as leachate from the landfill, this study concentrates on the laboratory phase of the overall program, which includes (1) determination of the dispersion coefficients of the various contaminants through the clay and (2) prediction of the migration profiles of the various contaminants as a function of pore volume displacement. While prediction verification is obtained using pore volume displacement as the control variable, establishment of this control variable with associated time characteristics, which will be integrated with the field monitoring system and test results, will be reported at a later time.

Material and Methods

To study the effectiveness or utility of the natural sensitive soil as a containment material, soil samples were obtained from the landfill area, at a point sufficiently remote from the actual disposal site. The typical composition and properties are given in Table 1, and the chemical analysis of the pore fluid, using the saturation extraction method, is given in Table 2.

TABLE 1—*Soil composition and properties.*

Parameters	Value	Composition by X-ray Analysis, Given in Decreasing Abundance
Liquid limit, %	65	
Plastic limit, %	26	feldspar
Natural water content, %	62	illite
Specific gravity	2.67	quartz
Natural dry density, Mg/m^3	1.39	kaolinite
Natural wet density, Mg/m^3	2.17	horneblende
Void ratio	0.9	chlorite
Cation exchange capacity, meq/g of soil	60/100	dolomite
Permeability (distilled water as permeant), m/s	10^{-9}	...
Grain size analysis, mm	$D_{50} = 0.8$	...
	$D_{10} = 0.1$	...

TABLE 2—*Soil pore fluid analysis.*[a]

Component	Amount, mg/L
HCO_3	180
Cl	170
Na	130
K	14
Mg	29
Ca	22
TOC	50
pH = 7.5	

[a]Heavy metals analysis, using the atomic adsorption technique showed that heavy metals were below detectable limits.

The leachate used in the laboratory study, as a control permeant solution, was collected directly from the basins designed to collect the leaching solution from the landfill (Fig. 1). The leachate was collected with a suction pump and put into plastic containers. Samples were collected from a number of points within the leachate basin, and representativeness was ensured by mixing the samples. To ensure that the composition of the leachate solution used in all the laboratory tests remained constant, a large supply of the leachate solution was collected and stored in plastic containers in a constant temperature room. The chemical analysis of the test permeant is given in Table 3, which is an average of three different samples.

Test Procedure

The test procedure for leaching tests consisted of using leaching columns 0.1 m diameter by 0.1 m high as shown in Fig. 2. Three complete test series, each consisting of four replicate samples, were structured for testing, using the test scheme shown in Fig. 3. In the first cell, after completion of passage of one pore volume of leachate, the test sample was removed and sectioned into six layers for analysis. In each of the other cells, prescribed volumes of leachate were also leached through the samples. The prescribed pore volumes passage of the leachate were one, two, three, and five, respectively. Using the natural soil and the permeant collected from the landfill site, the consistancy of three series is shown in Table 4.

As previously noted, following termination of the specified leaching test, the test sample was sectioned into six layers and the soil solution in each layer analyzed for both extractable and soluble ions. The extractable cations (sodium, potassium, calcium, and magnesium) were determined using the silver thiourea method of Chabbra [*3*]. The soluble cations, anions (Cl, CO_3, HCO_3) and heavy metals (iron, zinc, copper, and lead) were determined from pulverized samples. The sample was mixed with water to form a slurry until the saturation point was reached.

TABLE 3—*Analysis of leachate collected at landfill site for use in controlled laboratory leaching tests.*

Parameter	ASTM Test [*1*]	Concentration, mg/L	Standard for Drinking Water, mg/L [*2*]
BOD	D 888	450	40
COD	D 1252	860	100
TOC	D 2579	190	...
TC	D 2579	289	...
Oil and grease	D 4281	24	15
Phenol	D 1783	0.04	0.02
Total iron	D 1068	5.0	17
Mg	D 511	350	150
Ca	D 511	180	200
K	D 4192	16	...
Na	D 4191	140	270
NH_3	D 1426	20.0	0.5
Cl	D 1253	190	250
CO_3	D 513	0.0	...
HCO_3	D 513	303	...
pH	D 1293	6.8[a]	...
Specific electrical conductivity	D 1125	2.7×10^3 [b]	23.0[b]
Zn	D 1691	2.5	5.0
Pb	D 3551	1.0	0.05
Cu	D 1688	1.7	1.0
Total coli per 100 mL	D 3508	1100	2400

[a]PH units.
[b]In $\mu S/cm$.

The organic load was measured for the column effluents and pore water as total organic carbon (TOC). TOC measurements are considered in the present study because of the advantage over chemical oxygen demand (COD) and biological oxygen demand (BOD) as the latter methodologies may be significantly biased by the presence of reducing agents, refractory compounds, or toxic materials [*4*].

Results and Discussion

Migration of Heavy Metals

In the clay soil system, heavy metals may (1) occur in ion exchange sites, (2) be incorporated into or on the surface of crystalline or noncrystalline inorganic precipitates, (3) be incorporated into organic compounds, or (4) be in the soil pore solution. Most investigators have recognized that heavy metals occur predominantly in a sorbed state. Because of their low solubility, movement of heavy metals in soils has generally been considered to be minimal [5].

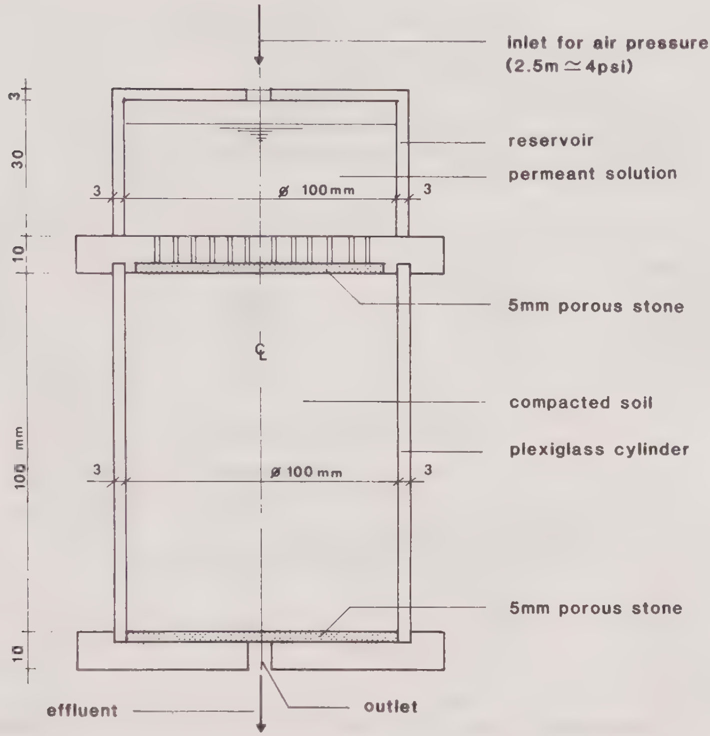

FIG. 2—*Schematic representation of laboratory leaching cell used in the study.*

Figure 4 shows the effluent relative concentration in the leachate, for heavy metals, zinc, lead, copper, and iron, as a function of pore volume passage. The other constituents, such as nickel, chromium, and arsenic, were found to be below the detection limits. Note that because of the need to maintain brevity in presentation of results (to meet page limitations), only representative results are shown. The results show that significant amounts of heavy metals were retained in the top portions of the soil samples, as seen in the concentration profile depicted in Fig. 5, for example, for iron. The profiles for the other heavy metals (not shown in this paper) exhibit similar characteristics. Table 5 gives the mean attenuation number for the metals. It is pertinent to note that chemical analysis of the sectioned columns confirms the large accumulation of all four heavy metals in the surface layers of each column. While this might be attributed to cation exchange replaceability, precipitation or filtration mechanisms or both appear to be a more plausible cause. Precipitation could involve formation of heavy metal hydroxides or carbonates, brought about by the relatively high pH found in the column effluents. The average pH value of the influent leachate was 6.90, while the average pH of the column efflu-

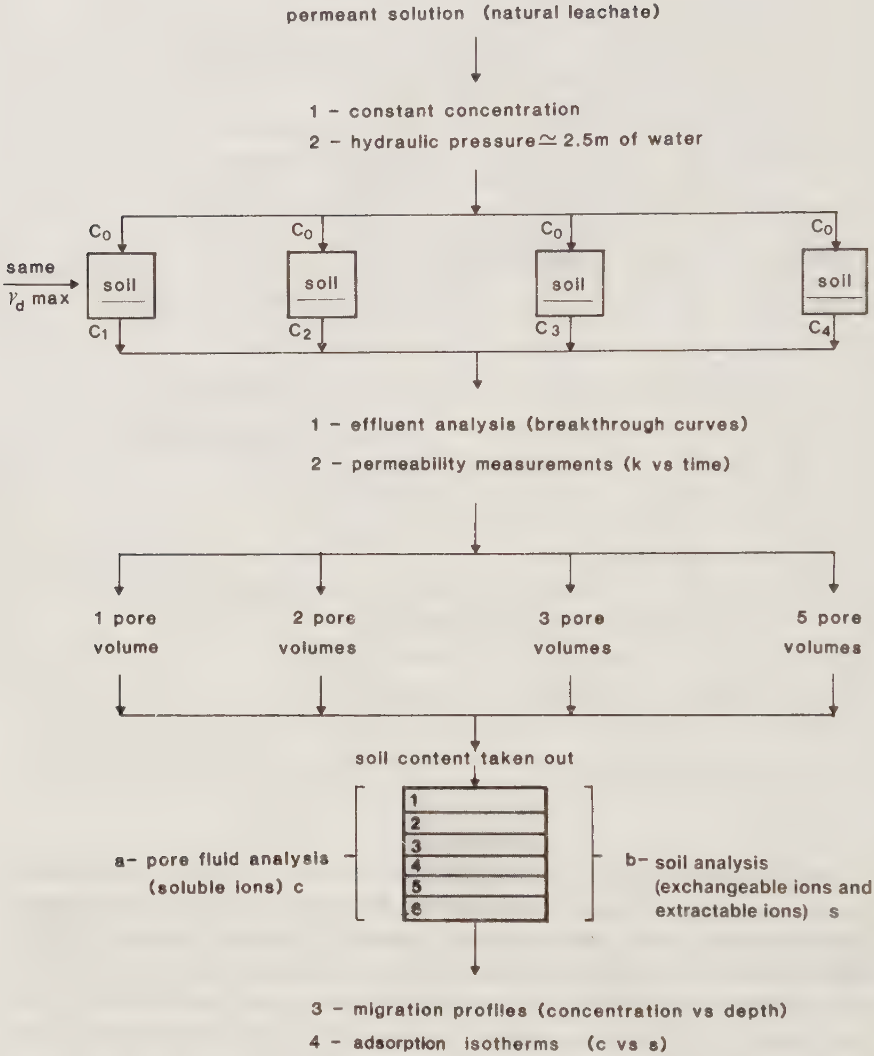

FIG. 3—*Test scheme used in the study.*

ents rose to 8.50. The increase in pH could result in precipitation of heavy metals from solution in the columns. These results agree well with previous determinations of many investigators, such as Griffen and Shimp [6], Bagchi [7], and others.

In summary, the migration of heavy metals appears to be limited through attenuation by more stable fractions, through such mechanisms as coprecipitation with iron oxyhydroxides and incorporation in silicate lattices. There is

TABLE 4—*Consistancy of three series using natural soil and the permeant collected from the landfill site.*

Series	Water Content, % (average)	Degree of Saturation, % (average)	Compaction, Blows/Layer
I	35	94	25
II	30	96	35
III	32	94	25

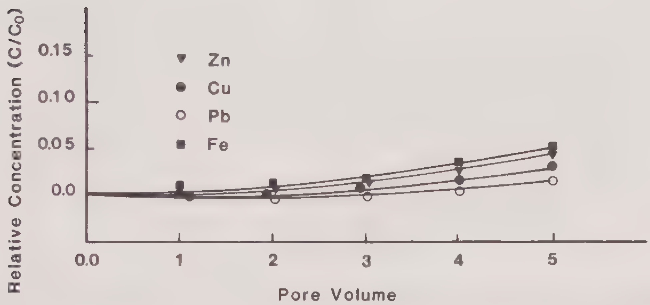

FIG. 4—*Relative concentrations of heavy metals (studies) in solution collected after leaching - as a result of pore volume passage of leachate.* C_0 *refers to initial concentration in the leachate.*

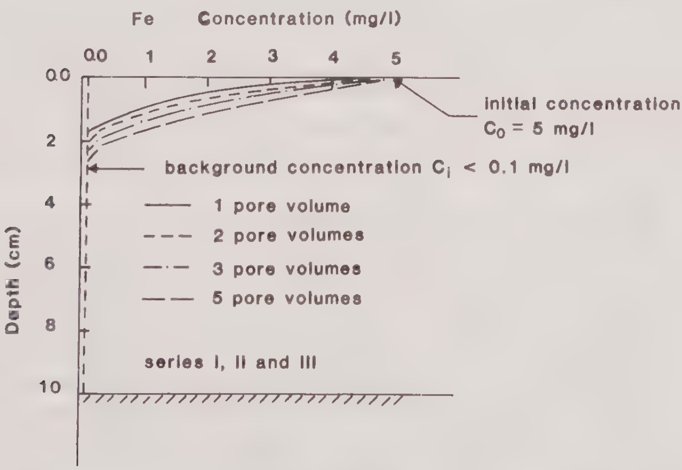

FIG. 5—*Iron concentration profile on test samples as a function of leaching with various pore volumes.*

TABLE 5—*Mean attenuation number (ATN).*[a]

Chemical Constituent	ATN for Series I	II	III	Average ATN
Pb	99.0	99.0	99.0	99.0
Zn	98.0	98.0	98.0	98.0
Cu	99.0	99.0	99.0	99.0
Fe	97.0	97.0	97.0	97.0
Na	−125[b]	−112	−100	−112.3
K	15	10	4	9.7
Ca	30	30	43	34.3
Mg	14	19	25	19.3
TOC	22	9	7	12.7
Cl	5	13	2.5	6.8

[a]Mean attenuation number (ATN) is the area under the breakthrough curve (relative concentration versus pore volumes relationship) subtracted from the total area that is bounded by five pore volumes and relative concentrations between 0.0 and 1.0 and expressed as percentage [*6*].

[b]Minus sign indicates elution.

no recognized significant difference in heavy metals migration through the three series studied.

Migration of Cations

Analysis of the pore fluid chemistry of the natural sensitive clay shows that the pore fluid is rich in sodium while other cations such as potassium, calcium, and magnesium are present only in low concentrations, as shown in Table 2. Some of the typical experimental results of the effluent cation concentrations for Series I, II, and III are shown in Figs. 6 and 7, for example, for sodium and calcium, with the corresponding migration profiles as shown in Figs. 8 and 9.

Figure 6 shows negative attenuation or elution of sodium from the column after passage of two pore volumes of leachate. The relative concentrations of greater than 1.0 indicate that sodium is eluting from the columns at higher concentrations than the influent leachate concentration. To a lesser extent, the results are somewhat similar for potassium while calcium shows no elution, even after passage of five pore volumes. This latter phenomenon is shown in Fig. 7. The cations attenuate mainly through cation exchange replaceability. The amount of reduction in concentration of a given element as it passes through the soil column is reflected by the extent to which the relative concentration remains below unity. For a given cation, with different initial soil conditions, the reduction in relative concentration with pore volume passage changes with the water content at which the clay soil was compacted.

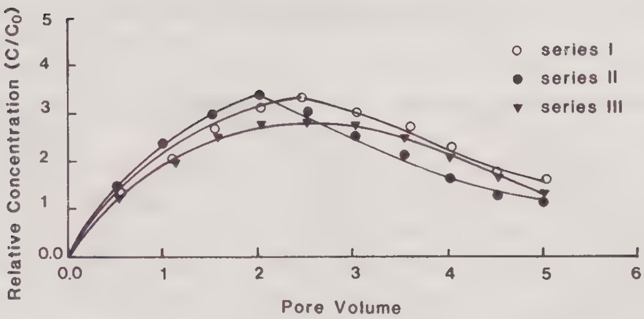

FIG. 6—*Relative concentration of sodium in solution collected after leaching, as a result of pore volume passage of leachate.*

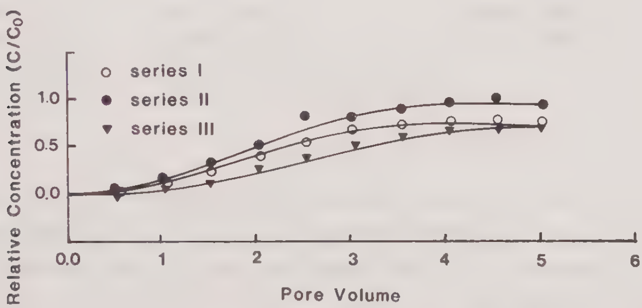

FIG. 7—*Relative concentration of calcium in solution collected after leaching, as a result of pore volume passage of leachate.*

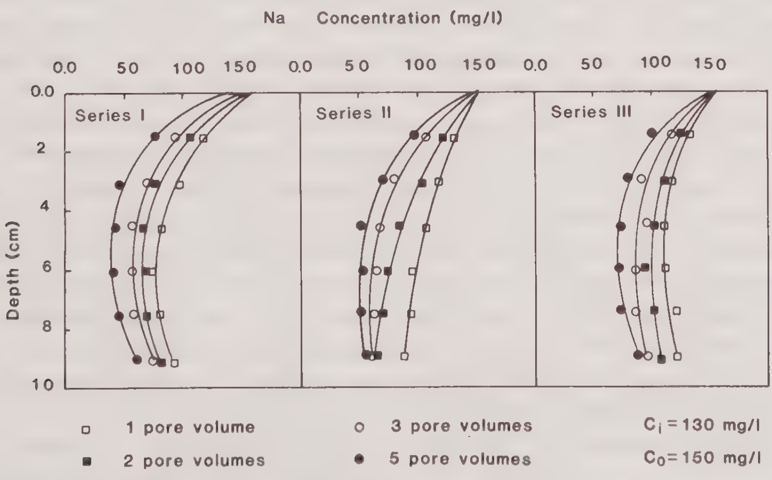

FIG. 8—*Sodium concentration profile distribution in soil columns.*

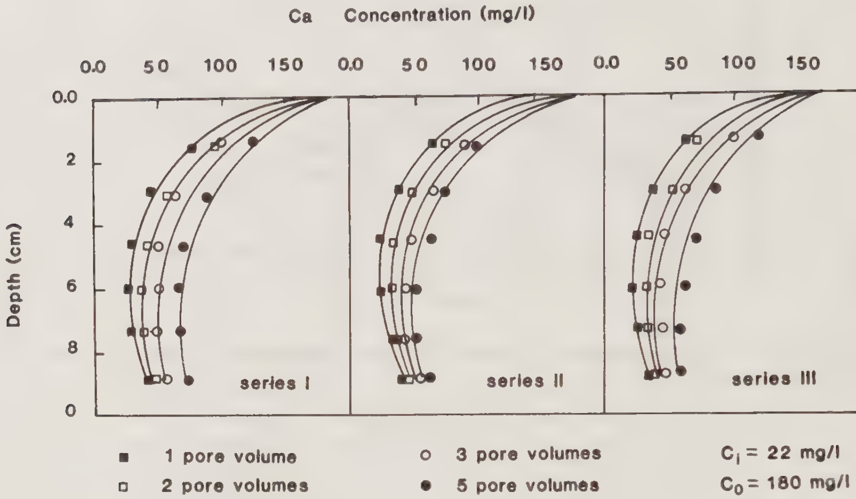

FIG. 9—*Calcium concentration profile distribution in soil columns.*

The test results indicate that the breakthrough points for the different cations studied fell at an average value of about 2.5 pore volumes for Series II and III. However, for Series I, the value shifted towards 3.5 pore volumes. Table 5 shows that in comparison to the heavy metals, the cations are less attenuated as the leachate passes through the soil.

Figure 8 shows the sodium ion distribution profiles for Series I, II, and III. This indicates that elution has progressed further in Series III apparently as a result of the slightly lower initial water content of the soil. The results appear to be complicated by the bottom boundary condition effect. It would appear that perhaps some void plugging might have occurred at the bottom boundary, as witness the increasing sodium concentrations at the bottom layers of Series I and III tests. Much work remains to be done to further elaborate on this phenomenon. Perhaps other considerations can also be entertained.

One would need to consider the cation exchange process between calcium, magnesium, and sodium, that is, the replacement of the sodium ion in the exchangeable sites by calcium and magnesium to balance the charge deficit that occurs by the elution of sodium ions (leached out), as shown in the results (Fig. 9) depicting the migration profiles of calcium. This is perhaps similar to the observations made by Crooks and Quigley [*8*] for results of calcium and magnesium migration in their studies, suggesting a requirement to balance the charge deficit that occurs by the elution of Na and Cl ions.

Comparison among the three series studied shows that it is reasonable to assume that any rearrangement of the configuration of the matrix would be minimal and the major change in permeability will arise from the changes in

ionic distribution associated with changes in exchangeable cations and electrolyte concentrations [*9*].

Movement of Organic Substance

Figure 10 shows the attenuation observed for the organic load contained in the leachate as it passed through laboratory columns containing the natural clay (Series I, II, and III). Unlike other contaminants, these organic compounds are not considered as ionic species. They represent a group of compounds that can be oxidized biologically or chemically. Little attenuation was found for the organic load measured as total organic carbon (TOC) (Table 5). The breakthrough point for TOC can be observed at an average value of about 2.5 pore volumes.

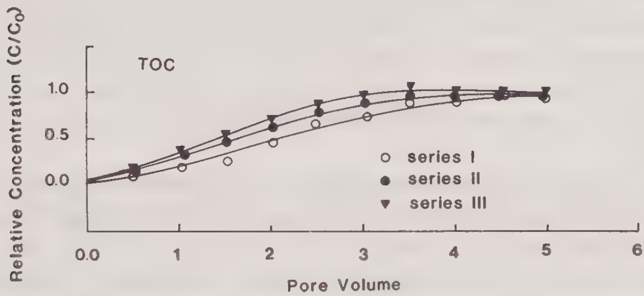

FIG. 10—*TOC relative concentration in solution collected after leaching, as a result of pore volume passage of leachate.*

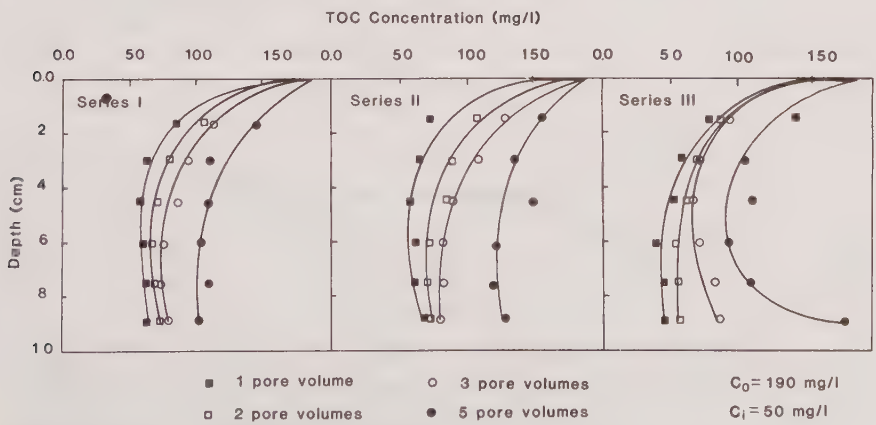

FIG. 11—*TOC profile distribution in soil columns.*

Figure 11 shows the TOC migration profiles for Series I, II, and III. In these series of column experiments, the landfill leachate, with an initial TOC value of 190 mg/L was passed through the clay columns under anaerobic conditions. From 40 to 50% of TOC removal was observed after six months of inflow exposure. The minor differences observed in Series I, II, and III can be due to the variations in individual samples.

Movement of Chloride Ions

Chloride attenuation was relatively low (only 6.5%, Table 5). This low attenuation is not surprising, because chlorine is considered to be a mobile non-interacting anion in soil systems. The low chlorine attenuation is generally not a function of the type or amount of clay mineral present. It can be attributed to the process of physical dispersion in the soil, with perhaps a small amount of interaction at anion exchange sites on the clay, or other chemical reactions.

The breakthrough point of chloride in Series III has been observed at about 1.5 pore volumes. However, for Series I and II the breakthrough points are at about 2.5 and 3 pore volumes, respectively (Fig. 12). This may be attributed to the change in moisture content that influences the diffusion in the clay-water system.

The results shown in Fig. 12 suggest that migration has progressed further in Series I and II than Series III. The chloride profiles indicate a larger concentration of chloride than sodium (for example) at each depth, which is not balanced by the sodium concentration present. This charge balance is maintained by migration of natural calcium and magnesium originally contained in the leachate, as suggested by the profile results for calcium and magnesium (Fig. 9), which indicates large increases in calcium and magnesium concentrations above the initial concentration.

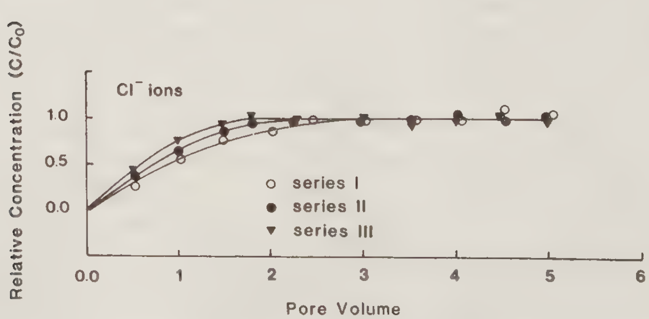

FIG. 12—*Cℓ relative concentration in solution collected after leaching, as a result of pore volume passage of leachate.*

It was noted that the normalized nonreactant chloride ion concentrations and normalized TOC concentrations for soil column effluents followed essentially the same breakthrough curve pattern (Figs. 10 and 12). Such an observation supports the TOC results, which indicate the low absorption capacity of the clay to the organics. This appears to support the results from Soyupak [*10*] who suggested that the equilibrium adsorption values for his clays were always less than 1.0-mg COD/g soil for COD values as high as 20 000 mg/L.

In summary, the likely reason that chloride showed no evidence of sorption and delay in breakthrough to input concentrations can be attributed to physical dispersion.

Theoretical Analysis

The physical processes of molecular diffusion and mechanical dispersion can both be treated as a Fickian type spreading mechanism. The two mechanisms can be treated together in terms of a single hydrodynamic dispersion coefficient D. The mass flux F is given by

$$F = \Theta V c - \Theta D\,(\partial c/\partial x) \tag{1}$$

where c = concentration of the contaminant, V = average pore-water velocity, and Θ = pore fraction (effective porosity) or the volumetric water content.

The first term on the right-hand side of Eq 1 refers to convection transport and the second term refers to the dispersive transport. The negative sign before the dispersive term indicates that transport of the contaminant is in the direction of decreasing the concentration gradient, whose x is the distance from the contaminant source.

Considering the mass balance condition

$$\frac{\partial \Theta c}{\partial t} = -\frac{\partial F}{\partial x} \tag{2}$$

Combining Eqs 1 and 2 gives

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) - \frac{\partial}{\partial x} V c \tag{3}$$

Equation 3 is the dispersion-convection equation in its one-dimensional form. In the present study the numerical solution of Eq 3 is performed using the finite-difference technique, similar to that used previously by Lai and Jurinak [*11*].

Comparison and Prediction

To test the prediction method, one can work with the dispersion coefficients, calculated from the test results obtained after leaching with one or more pore volumes of the leachate. Instead of assuming that the dispersion coefficients represent average values throughout the test samples, for the various individual contaminant components, the procedure followed recognizes that interactions established between the contaminant and the soil will cause continuous alterations in the transmissibility characteristics of the soil. Thus, it was decided that dispersion coefficients should be calculated for individual layers in the soil samples, and for each pore volume passage of the contaminant, using test Series III as the control samples. Using this test series, and the finite-difference scheme

$$\frac{C_i^{J+1} - C_i^J}{\Delta t} = D\,\frac{C_{i+1}^J - 2C_i^J + C_{i-1}^J}{\Delta X^2} - V\,\frac{C_{i+1}^J - C_{i-1}^J}{2\Delta x} \tag{4}$$

the dispersion coefficients can be calculated for different time and depth intervals. The results obtained can be typically represented (for example, for Cl) as shown in Fig. 13. The time intervals shown in the figure represent the time taken for leaching through one pore volume for each of the layers used in the calculations. The procedure permits determination of the variation of the dispersion coefficient with depth and with increased passage of the leachate.

Using the values for D computed from test results of Series III, taking note that these values vary throughout the length of the test sample and with the number of pore volumes of leachate, prediction of the contaminants profiles established in Series I and II can be attempted. These profiles can be compared with actual measured values obtained as shown in Fig. 14.

Comparison between predicted and measured profiles for various contaminants can be made, additional to the ones shown in Fig. 14. The immediately apparent observations concern the sensitivity of profile development and matching with the values of D used. By using the values for D calculated from Series III for the appropriate pore volume leached (identified as the "exact method"), it is seen that correspondence between predicted and measured values for Series II and III is highly acceptable. However, if one uses only the average D values, as is the normal procedure, poor correspondence between computed and actual measured profiles is established. This is shown in Fig. 14, where the average three and five pore volume values for D used in the computed profile is shown in comparison with the profiles determined, using the exact method, and the actual measured values. The values for D for the exact method were taken directly from Fig. 13 (from Series III) and used for the appropriate depth and pore volume passage.

The point of interest in making predictions of contaminant migration capability in a particular soil system obviously centers around the dispersion coef-

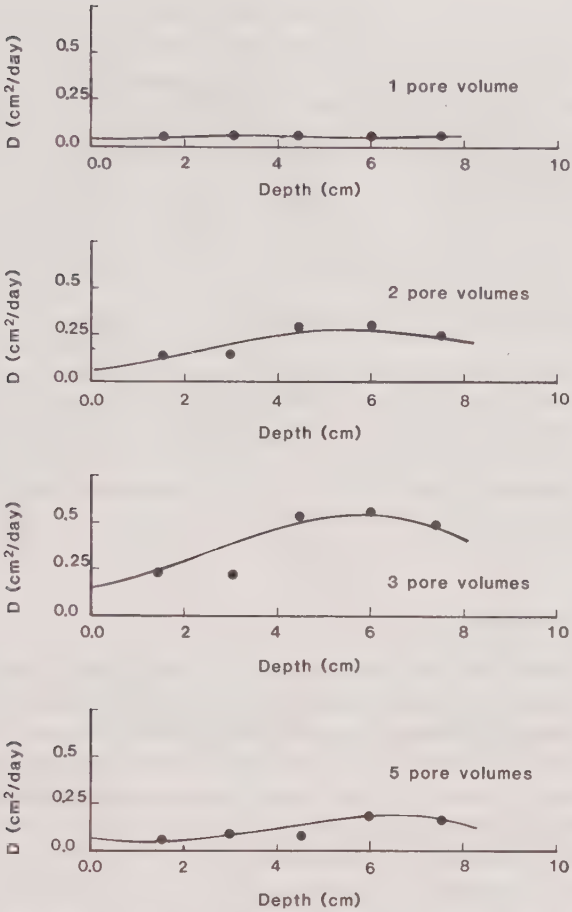

FIG. 13—*Dispersion coefficient* D, *calculated from Series III, as a function of pore volume passage and depth of soil column.*

ficients relating to the specific components in question. While calculation procedures can be mounted, dependent on the physical model chosen to represent the case at hand, the problem of "representativeness" of the D value obtained rests with choice of time span taken to assess leachate movement and attenuation. It is indeed clear that the D values will change with continued intrusion of the contaminant, not only because of alterations in the buffering capacity of the soil, but also because of the various possible transformations that could occur. Thus a fixed value for D for a particular contaminant, and for a specific soil type, is fictitious. What is needed is the mapping of variation of D values, performed in terms of time and space, or with respect to pore volumes and space.

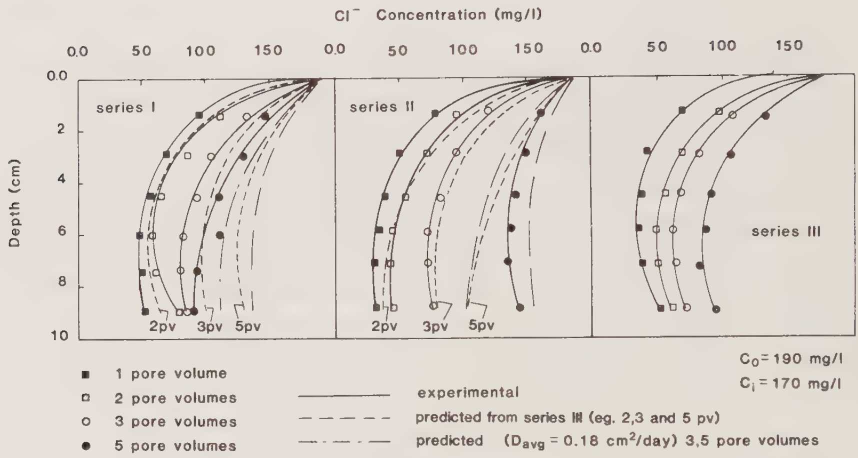

FIG. 14—*Comparison of predicted and measured Cℓ concentration profile in Series I and II, using* D *values obtained from Series III results (Fig. 13).*

Concluding Remarks

The test results for the study on the early migration of specific contaminants in a sensitive soil containment basin, using the soil in-situ as part of the clay liner, show that the heavy metals studied tend to be significantly attenuated in the upper layers of the clay. Mechanisms of coprecipitation and fixation appear to be reasonable candidates for explanations regarding attenuating capability of the soil. Insofar as migration of the various salts, these appear to be considerably less attenuated.

The buffering capability of the soil continues to change with passage of the contaminant, rendering it necessary to map changes in the specific dispersion coefficients with time, space, and pore volume passage of the particular contaminant. Unless this is established, prediction of contaminant migration cannot be reasonably made to accord with field expectations.

Acknowledgments

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Effect of Pore Fluid pH on the Dynamic Shear Modulus of Clay

REFERENCE: Du, B. L., Mikroudis, G. K., and Fang, H.-Y., **"Effect of Pore Fluid pH on the Dynamic Shear Modulus of Clay,"** *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 226–239.

ABSTRACT: This paper presents the laboratory test results on the dynamic shear modulus of clay mineral mixture with sand under dynamic torsion loading. Various pore fluids, as reflected by pH values ranging from 2.0 to 12.0, were introduced in the soil mixtures. Both shear modulus and maximum shear modulus were computed. Consolidation pressures varying from 34.5 to 276 kPa were used. All test results are presented in graphical and tabulated forms. Comparisons of various pH values with normal conditions are made. Finally, physico-chemical concepts are used to examine the soil-pollutants interaction.

KEY WORDS: soil dynamics, hazardous wastes, geotechnology, testing, instrumentation, composite materials, physico-chemical properties

The shear modulus of soil is one of the fundamental soil parameters required for the analysis of the response of soil and soil-structure interaction under dynamic loading. In recent years, many hydraulic structures, reservoirs, and river banks require seismic resistance considerations. However, these considerations are based on soil parameters under normal conditions where the contact pore fluid is not polluted. Unfortunately, in actual cases the contact water, in general, has some degree of pollutants caused by various liquid, solid wastes, and acid rains [*1*,*2*]. Therefore, the dynamic behavior of soil under normal conditions may be somewhat different in comparison to polluted water. Because of the complex nature of soil pollution, the terms

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"pollution" or "pollutant" are loosely used in this paper. These terms will be reflected in terms of the pH solution in the pore fluid or the ion characteristics of the solution. Water of very low or very high pH is considered polluted and could be hazardous for living organisms. This paper presents initial laboratory tests on how pore fluids with variable pH, which are representative of many hazardous materials, affect the dynamic shear modulus of clays [1]. A dynamic torsion device [3,4] is used for the study. Two clay minerals mixed with various percentages of fine sand are used. One is bentonite and the other is kaolinite. These two clay minerals are commercially available. The polluted water, as reflected on pH values ranging from 2.0 to 12.0, is introduced into the clay mixtures. Physico-chemical concepts are used to examine the soil-pollutants interaction under dynamic loads.

Experimental Study

Test Equipment

Laboratory cyclic torsional shear tests were conducted using a free vibration apparatus. Zeevaert [3] and Taylor and Parton [5] used this method to evaluate the dynamic shear modulus of sand and clay.

As Fig. 1 shows, the apparatus contains a triaxial cell, which has been modified in that a horizontal arm has been rigidly connected to the load arm. The load arm is supported by an intermediate bearing and is also securely fastened to the top platen.

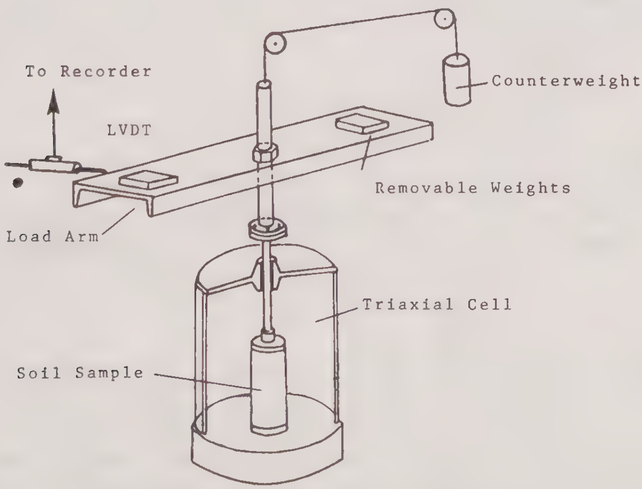

FIG. 1—*Free vibration-torsion test.*

The natural frequency of the apparatus can be adjusted by adding or removing weights mounted on the arm, placed symmetrical with the axis of the specimen. The weight of the arm and weights can be balanced by supporting them with a system of pulleys and counterweights. Thus, no vertical load is applied to the specimen, and the vertical as well as the horizontal stresses can be controlled.

On one end of the arm a linear variable differential transducer (LVDT) was mounted to measure the displacement of the arm. The LVDT was connected to an ultraviolet recorder which produced a trace of displacement versus time. A typical trace is shown in Fig. 2. To initiate the test a small impulse was given to the arm, and the arm/soil system experienced a decaying vibration.

The shear strains reported here and throughout this paper are strains at the beginning of the cycle calculated for a soil element at an effective radius of $^2/_3$ of the radius of the specimen. The range of the shear strain used in this test is from $10^{-2}\%$ to $4 \times 10^{-1}\%$.

The confining pressures in the triaxial cell were 28, 69, 138, and 276 kPa (5, 10, 20, and 40 psi). At first, the cell pressure of 35 kPa (5 psi) was applied and kept in for 3 h before the test begun. Then vibrations were applied to the specimen and measurements were taken. Following that, the cell pressure was increased to the next level of 69 kPa (10 psi) and kept in for an additional consolidation time of 1 h. Then the specimen was vibrated again, and measurements were obtained. The same procedure (increase the pressure to next higher level, allow 1 h for consolidation, test) was repeated for the subsequent cell pressures of 138 and 276 kPa (20 and 40 psi).

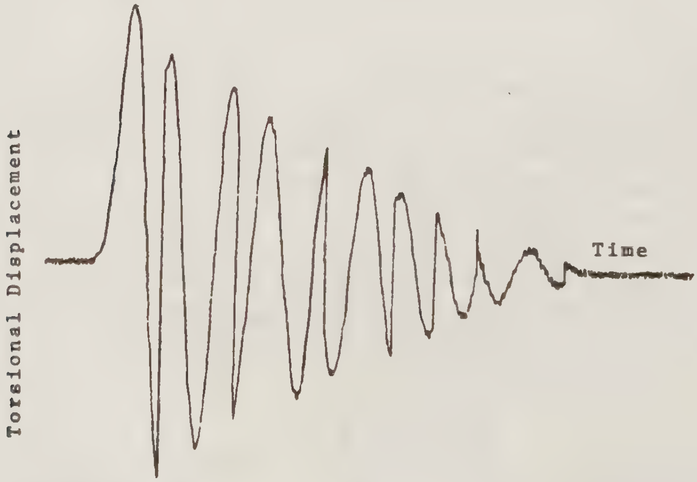

FIG. 2—*Typical record trace of torsional displacement against time from free vibration-torsion test.*

Method for Preparation of Soil Specimens

There are numerous hazardous materials, and it is impracticable to test them all. Thus, it is suitable to choose various pore fluids, that is, an alkaline fluid (sodium hydroxide with pH = 10, 12), an acidic fluid (hydrochloric acid with pH = 4, 2), and pure water (pH = 7). During these short-term tests, the pH of the solution remains the same after the experiment. However, in several cases of long-term permeability testing with hazardous permeants the authors have found that there is some change in pH. In our tests two kinds of clay sand mixture are used, one made of 15% bentonite and 85% Monterey No. 0 sand, and the other made of 15% kaolinite and 85% Monterey No. 0 sand. Five different kinds of solution (Table 1) are added, which have a 30% ratio to dry soil in weight of the bentonite mixture, and 15.2% ratio to dry soil in weight of the kaolinite mixture. After the soil has been mixed with the solution, the mixture and liquid will stand about 12 h for a reaction between soil and solution before they are tested. Specimens were in remolded condition. For all the samples the remolding involved a six layer moist tamping procedure on a membrane attached to the bottom platen. We tried to apply the same compacting method, the same compacting effort, and the same moisture content for all specimens, and thus we assume that the dry density is constant for all the specimens. Specimen dimensions were approximately 7.4 cm (2.9 in.) in diameter, and 14.0 cm (5.5 in.) in height. Contact between the specimen and the top and bottom platen was obtained by inserting razor blades in a radial pattern in the pore stones.

The Formulae and Parameters of the Apparatus

Shear Modulus G—According to Zeevaert [*3*] the shear modulus can be obtained from

$$G = [(\omega^2/(1 - D^2)]G_J \tag{1}$$

where

ω = undamped circular frequency, rad,
D = damping ratio,
$G_J = J_a h/I_p$

where

I_p = polar second moment of specimen = $\pi d^4/32$, and
J_a = polar moment of inertia of apparatus.

The polar moment of inertia of the whole apparatus consists of the sum of moment of inertia of arm, specimen, and rod. However, the polar moment of inertia of the rod and specimen are about 10^{-12} and 10^{-8} times, respectively,

TABLE 1—*Summary of properties of materials and pore fluids.*

Materials	Bentonite, %	Kaolinite, %
SiO_2	56.5	46.1
Al_2O_3	20.0	38.1
Fe_2O_3	4.8	0.55
CaO	1.8	...
MgO	4.0	...
K_2O	0.7	...
Na_2O	3.5	...

NOTE: Pore Fluids: The pH values of the solution of sodium hydroxide (NaOH) were 10 and 12; the pH values of the solution of hydrochloric acid (HCl) were 2 and 4; the pH value of the distilled water used was approximately equal to 7.

Clay Minerals: Commercially available clay minerals, the bentonite and kaolinite clays are used.

Sand: Monterey No. 0 sand.

smaller than the polar moment of inertia of the arm and therefore can be neglected. Also, for our testing the removable weights were not used. Thus the polar moment of inertia of the apparatus is approximately equal to

$$J_a = mL^2/12 \tag{2}$$

where

m = the mass of the arm and
L = the length of the arm.

The damping ratio D and the circular frequency ω can readily be evaluated from the record. Since the damping ratio is always less than 0.2 (as confirmed in our experiments),[3] we can neglect D^2. Also the damped frequency ω_D is related to the undamped frequency ω by the formula, $\omega_D = \omega(1 - D^2)^{1/2} \sim \omega$. Thus, since $D < 0.2$, the damped and undamped natural periods are approximately equal, and instead of ω we can measure the damped natural period T from the record and then evaluate ω through the relationship

$$\omega = 2\pi/T \tag{3}$$

Thus, finally, the formula to calculate the dynamic shear modulus directly from the record is

[3]As Table 3 shows the maximum D measured in the experiments was 0.2. Since the actual D of the soil is less than the D measured (which includes all other damping losses), it was reconfirmed that the damping of soil is indeed less than the assumed 0.2.

$$G = (G_{oJ}/T^2) \tag{4}$$

where $G_{oJ} = 4\pi^2 G_J = 32\pi mL^2h/3d^4$.

Damping Ratio D—According to Zeevaert [3] the damping ratio can be calculated from

$$D^2 = \Delta^2/(4\pi^2 + \Delta^2) \tag{5}$$

where the value of Δ is known as the logarithmic decrement and may be determined from successive amplitudes of the damped vibration

$$\Delta = \ln(\delta_n/\delta_{n+1}) \tag{6}$$

The values of D calculated from the test using Eq 5 have no relationship with the real damping for the soil, because this value includes the effect of frictional forces of the instrument during vibration. Although the exact value of the damping ratio for the specimen can not be found precisely, the relative values of damping ratios between different specimens allow for a comparison of the effects of different pore fluids.

Analysis of Test Results

The Shear Modulus of the Specimens of Kaolinite and Sand

This group of specimens was made of 15% dry kaolinite and 85% dry Monterey No. 0 sand with different solutions. There were solutions of pH = 2, 4 (hydrochloric acid solution), pH = 7 (water), and pH = 10, 12 (sodium hydroxide solution). All the specimens had the same water content (15.2%) and the same initial dry density. A typical record of this group is shown in Fig. 2, having characteristics of sand, which seems to have a little plasticity and a vibration with many peaks.

There are some figures that show the relationship between shear modulus G and shear strain γ with different pore solutions (Figs. 3 through 5), and shear modulus G and different pore solutions at cell pressure 276 kPa (40 psi) (Fig. 6). The curves in Figs. 3 through 5 are found by applying linear regression to the data points for $1/G$ and γ. It is shown that in the suitable range pH = 2 to 12, the shear modulus increases when the pH value decreases. According to Fig. 6 this result is observed for the acetic solution (pH $<$ 7). For the alkaline fluid (pH $>$ 7), however, the shear modulus first increases with decreasing pH and then unexpectedly drops.

The increase of shear modulus with decreasing pH is consistent with the Gouy-Chapman theory, which predicts the influence of pH value on the diffuse double layers and the structure of clay. The effect of pH can influence the thickness of the double layers in several ways. Changing the pH value could

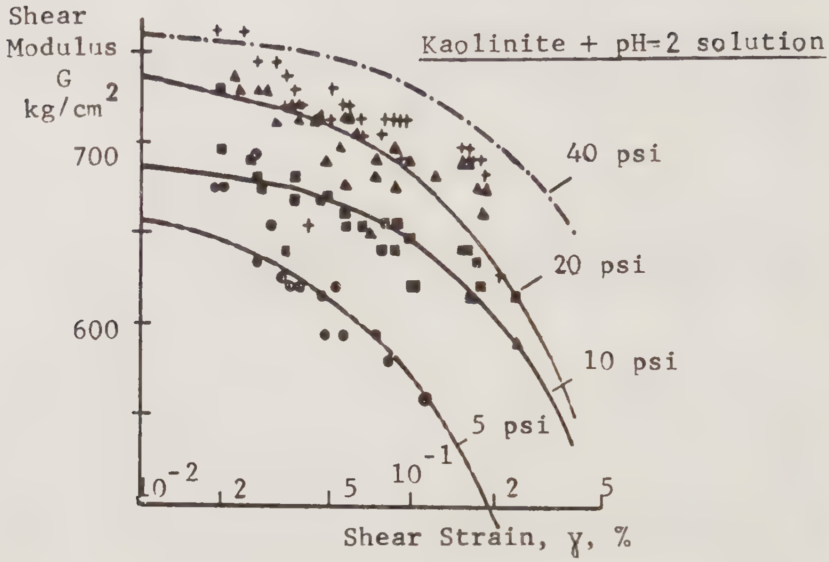

FIG. 3—*Relationship between shear modulus G and shear strain γ for pH = 2 solution.*

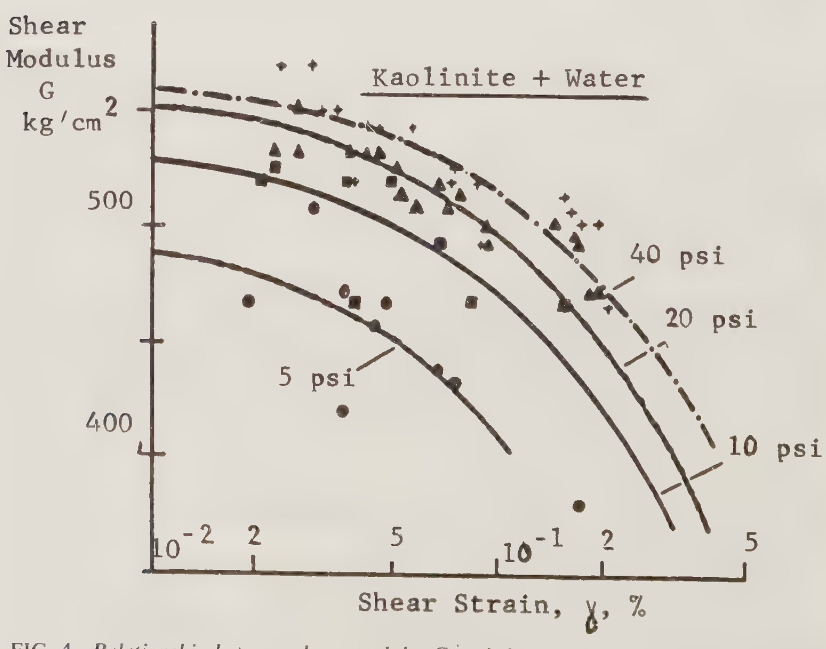

FIG. 4—*Relationship between shear modulus G and shear strain γ for pH = 7 solution.*

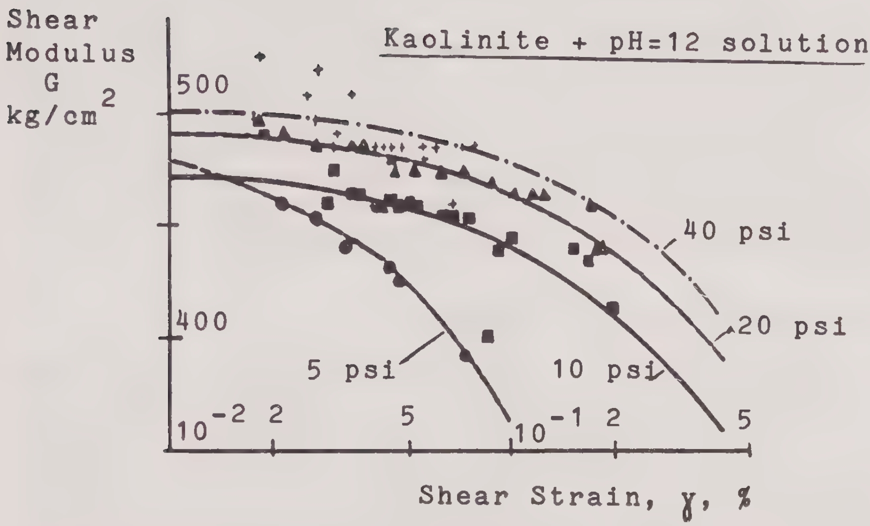

FIG. 5—*Relationship between shear modulus G and shear strain γ for pH = 12 solution.*

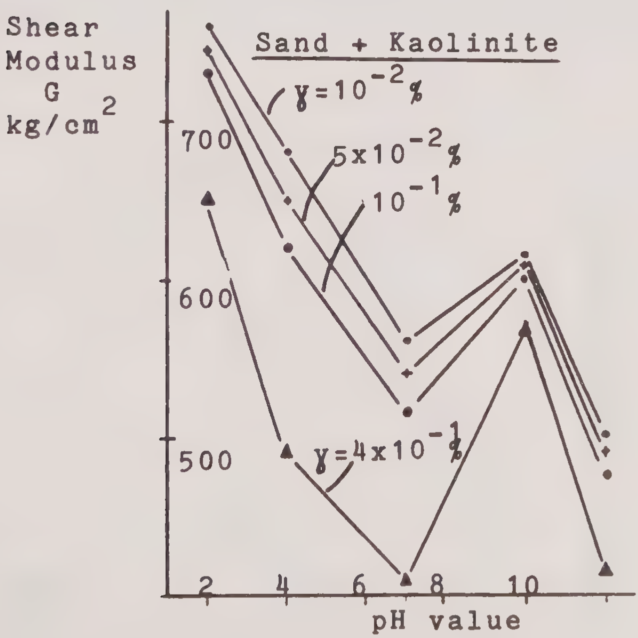

FIG. 6—*Relationship between shear modulus and different pore solutions at cell pressure 276 kPa (40 psi).*

affect the electrolyte concentration as well as the net negative charge on the clay particle by altering the extent of dissociation of the hydroxyl (OH^-) groups at the edges of the clay particle. High pH encourages the dissociation and increases the net charge, thus expanding the double layer. Thus, it makes the structure of clay more dispersed, and the shear modulus, including the dynamic shear modulus, decreases. Low pH discourages this dissociation, and causes a decrease in the net charge, therefore, causing a reduction in the double layer. A reduction in the double layer increases the tendency towards flocculation of the clay particles. Thus, it increases the shear modulus of clay.

The Specimens of Bentonite and Sand

This group of specimens was made of 15% dry bentonite and 85% Monterey No. 0 dry sand with different solutions. There were solutions of pH = 2, 4 (hydrochloric acid solution), pH = 7 (water), and pH = 10, 12 (sodium hydroxide solutions). All the specimens had the same water content (30%) and the same initial dry density. A typical record of this group is shown in Fig. 7, having characteristics of clay with a lot of plasticity for obviously moving the equilibrium position of vibration and for a fast attenuation of vibration. Thus, it is difficult to get reliable results.

There are some figures that show the relationships between shear modulus G and shear strain γ with different pore solution (Figs. 8 through 10), and shear modulus G versus pH value at cell pressure 276 kPa (40 psi) (Fig. 11).

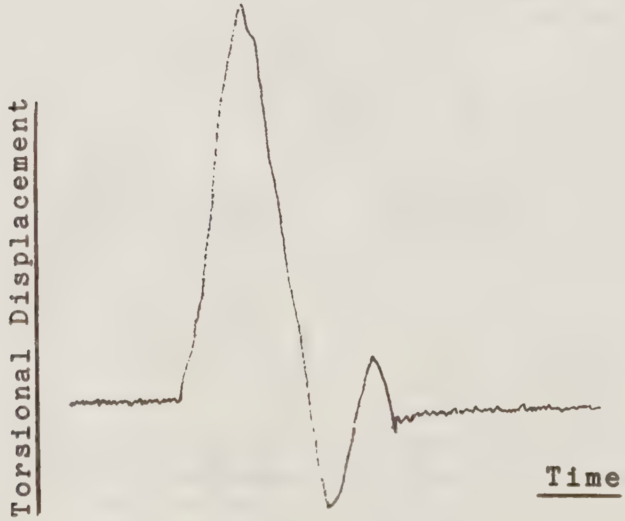

FIG. 7—*The typical recorder of vibration of sand and bentonite.*

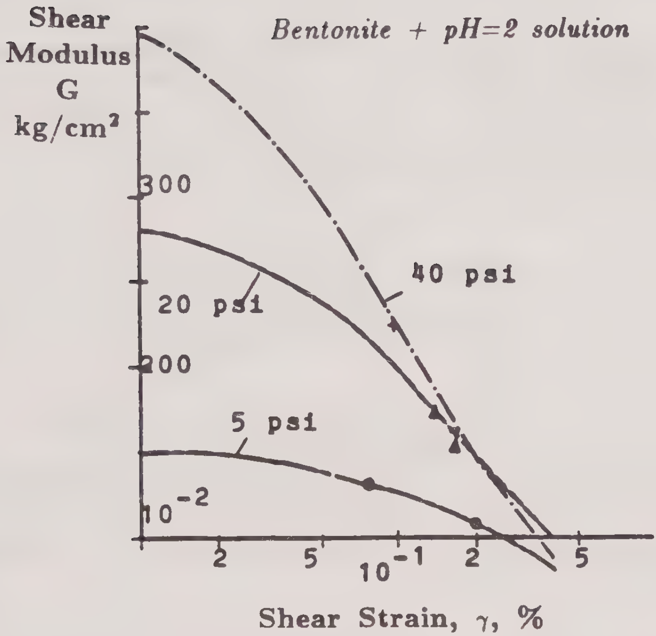

FIG. 8—*Relationship between shear modulus G and shear strain γ for pH = 2 solution.*

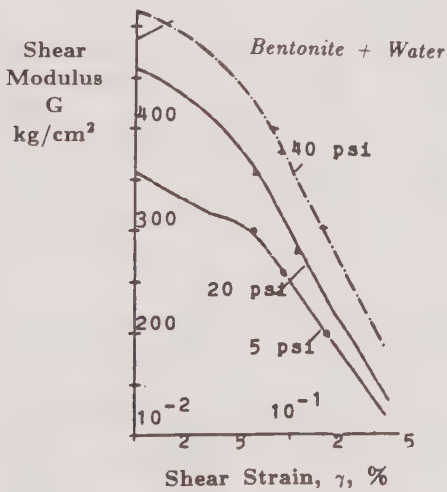

FIG. 9—*Relationship between shear modulus G and shear strain γ for pH = 7 solution.*

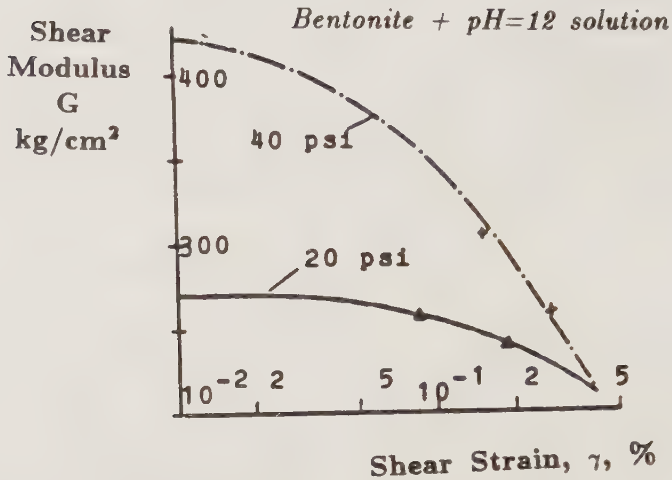

FIG. 10—*Relationship between shear modulus* G *and shear strain* γ *for pH* = *12 solution.*

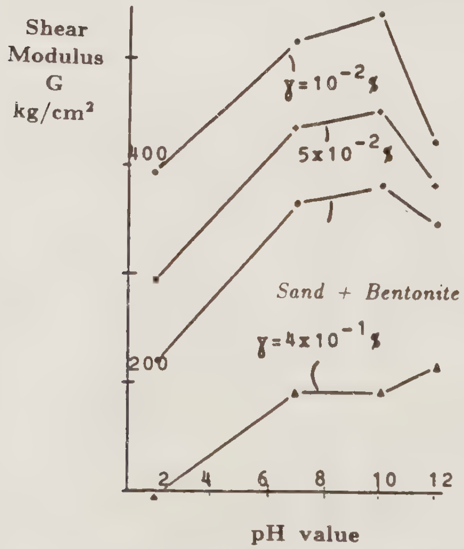

FIG. 11—*Relationship between shear modulus and different pore solutions at cell pressure 40 psi (276 kPa).*

Figure 11 shows that the relationship between shear modulus G and pH value for the bentonite mixtures is quite different than the one found for the kaolinite for some unknown reason. For the alkaline solution (pH > 7), the shear modulus changes slightly and shows a similar behavior to the kaolinite specimens with an initial increase followed by a decrease of shear modulus as pH decreases. However, for the acetic solution (pH < 7) when the pH value decreases from 7 to 4, the shear modulus is increased, and when the pH value continues to decrease, the shear modulus drops down fast. This result can not be explained with the Gouy-Chapman theory and similar reasoning to the one used for the specimens of kaolinite and sand.

Bentonite and kaolinite are quite different minerals however, as it is evident from Table 2. Thus, a difference in behavior between these two minerals for different pore solutions should be anticipated.

The Damping Ratio of the Specimens of Kaolinite and Sand

Only this group of specimens had enough vibration peaks on the records for calculation and analysis of the damping ratio. The other group made of bentonite and sand had a few vibration peaks (Fig. 7) and cannot be used since the visco-elastic model does not fit in these soil specimens. In Table 3 the shear strain and damping ratio are listed with 276-kPa (40-psi) cell pressure and different pore solutions.

The damping ratio D decreases with strain, and this tendency is opposite to some results coming from the dynamic triaxial instrument. As Table 3 shows,

TABLE 2—*Difference of properties between bentonite and kaolinite.*

Parameters	Bentonite	Kaolinite
Cation-exchange capacity	80 to 150	3 to 15
Thickness, A	10 to ~50	100 to ~1000
Specific surface, m^2/g	800	10

TABLE 3—*Relationship between damping ratio,* D, *and shear strain* γ *for different pore solutions of the kaolinite + sand specimen at cell pressure 276 kPa (40 psi).*

Parameters	pH = 2	pH = 4	pH = 7	pH = 10	pH = 12
γ, %	0.043	0.059	...	...	0.042
D	0.133	0.200	...	...	0.097
γ, %	0.097	0.101	0.092	...	0.066
D	0.069	0.120	0.096	...	0.098
γ, %	0.206	0.195	0.215	0.229	0.197
D	0.059	0.073	0.072	0.110	0.043

when the pH value varies from 4 to 10 the damping does not change very much, but outside this range it decreases, and more quickly for pH = 12.

Summary and Concluding Remarks

The influence of different pore fluids on the dynamic behavior of a sand clay mixture has been examined with two groups of sand-kaolinite and sand-bentonite mixtures, which show different tendencies:

1. For an acetic fluid (pH < 7)

(a) with samples made of kaolinite and sand the dynamic shear modulus increases when the pH value decreases from pH = 7 and
(b) with samples made of bentonite and sand the dynamic shear modulus decreases when the pH value decreases from pH = 7.

2. For an alkaline fluid (pH > 7), the dynamic shear modulus increases initially, but then decreases when the pH value decreases.
3. In the range of pH = 4 to 10 the damping ratio of kaolinite and sand remains roughly unchanged, and if the pH value is beyond this range the ratio will decrease.

According to present theories it is possible to explain an increase in the shear modulus with decreasing pH because of more flocculated clay structure or a decrease in the shear modulus with increasing pH caused by a more dispersed clay structure. We were unable to explain different trends than these on the basis of such simplified theories as the Gouy-Chapman theory. More research is needed in this area.

Acknowledgment

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Site Monitoring and Assessment

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Remote Sensing Methods for Waste Site Subsurface Investigations and Monitoring

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ABSTRACT: Detection and monitoring of subsurface contamination at waste disposal or storage sites can be expensive and uncertain with traditional sampling and measurement techniques. Remote sensing methods can greatly aid characterization of the subsurface and detection of contaminants in the vicinity of waste deposits. Inexpensive aerial remote sensing, such as photography or infrared scanning, can indicate subsurface contaminant movement and structure. Resistivity surveys and other surface remote sensor applications develop further details on subsurface geology and plumes. Most importantly, development of detailed vertical profiles with subsurface sensors provides indispensable data for ultimate characterization of the subsurface environment. Subsurface geophysical remote sensing techniques commonly used for deep subsurface characterization associated with petroleum or mineral exploration must be modified to be used effectively in the shallow depth range associated with surface disposal or storage sites.

KEY WORDS: geophysical surveys, remote sensing, subsurface investigations, aerial surveys, waste disposal, hydrology

First let us define remote sensing as used in this dissertation. It is the second of two meanings in common use:

1. A sensor, such as a pH probe, that is in contact with the material of interest and is connected to a distant (remote) recording instrument via a physical conductor or telemetry system.
2. A sensor, such as an airborne scanner, that is located at distance (re-

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mote) from the physical characteristic to be detected or measured and senses this parameter via electromagnetic radiation.

Usually this electromagnetic signal to the remote sensor is transmitted through the atmosphere or through the hydrogeological medium under study in subsurface investigations. The distance of the remote sensor-recorder from the target material may range from a few centimetres to many kilometres.

Remote sensing for waste site subsurface investigations and monitoring is particularly appealing for economy of money, time, and energy. Atmospheric and land surface contaminant detection and measurement with remote sensing technology can be relatively inexpensive compared to subsurface sampling and measurements with nonremote methods, when considerable effort is required to remove material to gain access to subsurface detection and measurement points.

There may be a tendency for an investigator to discard remote sensing as a site investigation tool as too expensive, too complex, or providing indefinite information. However, use of remote sensor data gathering methods can contribute valuable information to help the investigator design a less costly and more productive hole drilling operation, whether the purpose be for a one-time site investigation or long-term site monitoring. Once investigators decide to consider the option of using remote sensing, they should assure themselves that they have considered the full scope of remote sensing tools available as well as the integration of supplemental data sources. That is a key point we wish to emphasize.

Remote Sensing Techniques

Available remote sensing techniques for developing subsurface information can be classified as: (1) airborne, (2) ground surface, and (3) subsurface, or downhole. These classifications are based on the location of the sensor. In initial site investigation stages, aerial remote sensing, such as infrared photography and multispectral scanning, can provide valuable guidance for further remote sensor applications on the surface and ultimately for placement of soil and water sampling sites. Traditional geophysical measurement techniques, as commonly employed by the mining and petroleum industry for deep subsurface characterization, must be modified to be used effectively in the relatively shallow depth range associated with surface disposal or storage sites. In this manner, both surface-placed and borehole sensors may be employed to define geologic conditions and sense hydrologic properties, including detection of contaminant plumes. Applicable methods may include seismology, magnetometry, ground-penetrating radar, resistivity, and electromagnetic induction with surface instruments; and induction logging, neutron logging, gamma profiles, and fluid physics measurements from borehole sensors. Collection of gaseous emissions from soils and liquid extraction from

unsaturated soil zones are important for correlation with remotely sensed data. Longer term subsurface monitoring approaches include using optical fibers tipped with optrodes for laser induced fluorescence detection of contaminants. These sensors can be emplaced to various depths in low-cost small-diameter holes to round out a cost-effective approach to remote sensing of contaminants from hazardous waste sites.

The techniques to be used for site subsurface investigation or monitoring are dictated by the situation at hand, and in nearly all cases must be complemented or supplemented with other data collection techniques. Initial objectives for site investigations can include

(1) waste site discovery,
(2) site characterization (environment, geology, hydrology, and so forth),
(3) waste location,
(4) detection of waste or leachate movement,
(5) definition of waste or leachate movement boundaries, and
(6) contamination characterization (constituents and magnitude).

If the purpose is to discover sites that may be contaminating the subsurface, aerial sensing in the form of photography may be the only technique employed. If it is supplemented with data from other sources, such as citizen interviews and searches of construction permit records, business permit or license records, and geology and hydrology records, an effective site discovery and priority classification can be achieved [*1*].

Remote Sensing Applications

Our experience has shown that historical aerial photography obtained from city planners, agricultural agencies, and other private or government photography files can provide information dating back 20 or 30 years or more. This information is extremely helpful in locating possible waste disposal sites or observing disposal pits and practices at known sites over a period of years. In this manner, we have been able to precisely locate burial areas that have since been covered by urban development.

Once a waste site has been identified, some level of further investigation may be in order. (The site may be used for future planned waste disposal, as well as already existing waste disposal.) This may be a first-level investigation using only detailed interpretation of aerial photography to define site extent, topography, surface-to-surface contamination routes, type of waste storage, and disposal activity and procedures [*2*].

A second-level investigation may include surface remote sensing techniques in addition to aerial remote sensing, written record searches, and site operator or employer interviews. Here again, historical aerial photography can be extremely helpful. Aerial multispectral scan imagery may be employed to search for surface indications (for example, temperature and vegetation vigor

differences) of subsurface plumes. Surface-based sensors for resistivity mapping to define subsurface contaminant plumes, or magnetometry to locate subsurface waste containers may be employed.

A third-level investigation includes addition of downhole sensor techniques to produce more detailed definition of the subsurface geologic and hydraulic structure, as well as define the location and specific constituents of contaminants or leachate plumes. This third-level investigation may include chemical analysis of physical samples to complement the remote sensing data. The downhole sensing techniques may include gamma-gamma density logs, natural gamma logs, and induction logs (a "log" is defined as a record of sequential data). Subsurface logging, sometimes called borehole geophysics, includes recording types of material encountered at various depths during hole construction [*3*] and all techniques of lowering sensing devices down a borehole and recording some physical parameter that may be interpreted in terms of the subsurface geological and hydraulic structure. A matrix of applicable techniques for each level of investigation versus the investigation category is suggested in Fig. 1.

Aerial Techniques

Aerial photography does not always strike an investigator as a remote sensing technique. Because of its ready availability and simplicity, we believe it should be a standard part of any waste site subsurface investigation or monitoring program. At a minimum it provides a great deal of detailed information that cannot be viewed or gathered from any other single vantage point, and almost anyone can interpret the data provided to some extent. Surface conditions, surface features, surface geology variations, and surface horizontal and vertical relationships of natural and man-made features that provide information on possible subsurface structure and potential sources or routes of contamination to the subsurface saturated and unsaturated zones may be ascertained. Nontechnical publications are available that help an investigator develop basic skills in use of aerial photography specifically for waste site analysis [*2*]. More detailed information can be derived by skilled aerial photography analysts. Additionally, photogrammetric detail and surface elevation contours can be readily obtained with photography.

Acquisition of aerial photography can range in sophistication (and cost) from hand-held cameras with standard color film to high quality but low-cost vertical and oblique color or infrared film photography with cameras mounted in strap-on pods to light single-engine aircraft [*4*]. More costly vertical framing cameras, which produce state-of-the-art image resolution and mapping accuracy images on different specialized films using an array of filters, may also be used for sophisticated spectral analyses. The use of these films can provide sensitive indications of subsurface contaminant plumes that

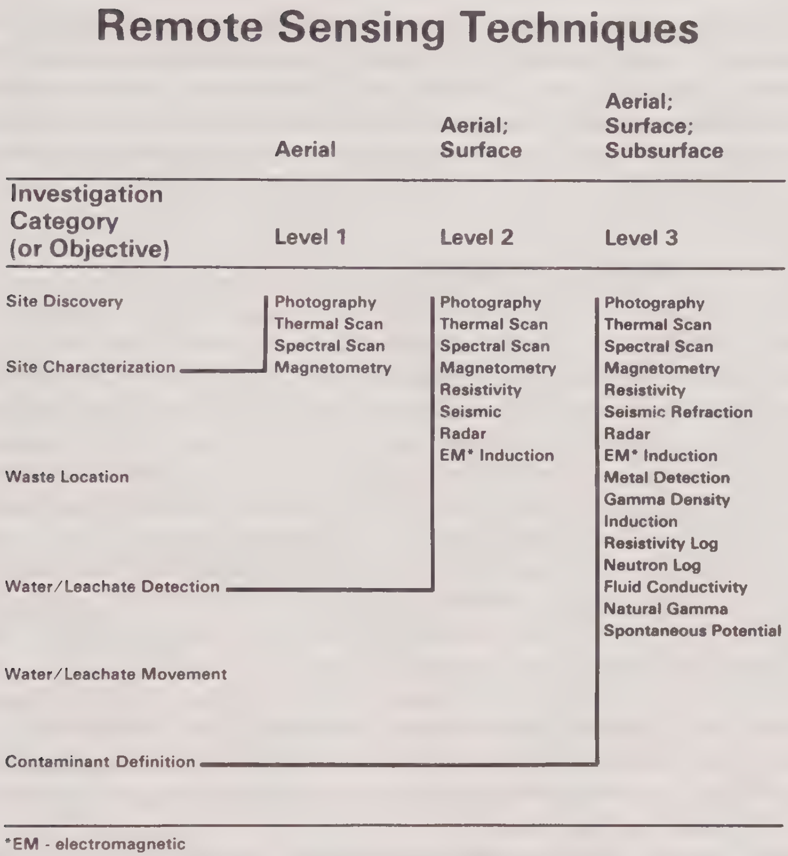

FIG. 1—*Applicable remote sensing techniques for waste site subsurface investigations.*

may be causing variations in surface vegetation or soil conditions. These kinds of information are extremely valuable in designing subsequent surface remote sensing surveys to define subsurface conditions further and for determining placement of drilled holes for subsurface remote sensors. Photography can also be an extremely valuable data base for long-term monitoring to detect surface changes that may indicate subsurface contaminant movement. Some basic study and planning of image size and resolution obtainable from various altitudes with various film sizes and cameras will greatly increase the effectiveness of photography eventually gathered. From our experiences in conducting photographic analyses of over 2000 hazardous waste sites over the past five years, film image scales of 1:2400 have been found to be most useful for general site detail definition without using enlargements or viewing magnification optics. A scale of 1:6000 has been found suitable when standard magnification equipment is available.

In selected instances, thermal scanning and multispectral scanning (that is, infrared through ultraviolet frequencies) can provide information on subsurface leachate transport by defining surface reflectance anomalies not visible in photography. For example, subsurface contaminant movement may create vegetation vigor fluctuations that are apparent only in scanner imagery.

Surface and Subsurface Techniques

The list of surface and subsurface techniques given in Fig. 1 is not an all-inclusive list of so-called geophysics techniques available for subsurface characterizations. Extensive texts are available that present detailed theory, operational, and data interpretation information on gravity, magnetic, seismic, electrical property, electromagnetic, and radioactivity methods [*5*]. There are a variety of techniques available with nearly each method. Various combinations of these techniques have been used for decades for mineral and petroleum exploration purposes. However, the applications are typically for relatively deep (hundreds to thousands of metres) characterizations and therefore need testing and probably modification to enable their use for the much shallower depths (a few metres to decimetres) associated with investigating and monitoring waste sites. The wastes are usually on or near the surface, and contamination is usually limited to areas near the surface. Methods evaluation studies by the U.S. Environmental Protection Agency and other investigators have helped to define these techniques to provide useful subsurface information, to develop standardized operating procedures, and to help assure the quality of data obtained.

Our experience has shown that different investigators using the same surface-based geophysical techniques may interpret the data obtained in different ways or obtain misleading data because of use of improper techniques for a given situation or information objective. Therefore, a reduced number of available surface and subsurface remote sensing techniques need to be considered [*6*]. Some investigators have concentrated on surface-based techniques [*7*], while others have focused on subsurface techniques [*8*]. In any case, our field research and that of others have shown that conventional hardware and procedural methods may need to be modified in order to produce useable data [*8*], and that proper training of operating personnel and data analysts is essential. In some, skill level must be extremely high [*9*].

Once a decision has been made via the Fig. 1 matrix approach as to the level of investigation to be conducted, further consideration of the type of information that will be useful is in order before a selection of techniques can be made. If detecting the location and extent of a suspected subsurface plume from an inorganic waste storage site is the objective, will subsurface geologic structure data be needed? Do buried containers need to be located? Is direct interaction with a saturated zone a possibility? To help the investigators fur-

ther, a technique versus information matrix, shown in Fig. 2, may be of value. This has been derived from our work and the work of several other investigators. However, there is a second step that is critical before a commitment is made to employ a given method, and that is to consider the limitations of a given method in terms of "range of effectiveness" from the sensor. Here again, experiences by other investigators are available to serve as a guide when using surface techniques (Table 1) [7]. All are readily affected by varying soil matrices, presence of saline aquifers and clay lenses, and cultural interferences, such as overhead power lines and buried cables or sewers. The

	Technique												
Information Objective	Radar	Electromagnetics	Resistivity	Siesmic	Metal Detector	Magnetometer	Natural Gamma Log	Electric Log	Density Log	Induction Log	Neutron Log	Thermal Flowmeter[a]	Spontaneous Potential
Lithology		●	●	●			●	●	●	●			●
Formation fluid			●					●		●	●		●
Porosity							●		●		●		
Clay or shale content							●	●	●				
Permeability							●		●	●		●	
Ground water direction, velocity												●	
Buried trenches with metal	●	●	●	●	●	●							
Buried trenches without metal	●	●	●	●									

[a]Not a remote sensor in terms of this paper, but readily provides a critical piece of information for any subsurface investigation.

FIG. 2—*Surface and subsurface sensing techniques versus information objective.*

TABLE 1—*Typical "range of effectiveness" for surface remote sensing techniques* [7].

Technique	Subsurface Range, m
Resistivity	1 to 100
Ground-penetrating radar	0 to 5
Electromagnetic induction	0.75 to 60
Metal detection	0 to 3
Seismic refraction	1 to 30
Magnetometry	0 to 5

"range of effectiveness" for downhole techniques is somewhat less, limited to a few metres from the hole.

If site subsurface characterization is the goal of an investigation in order to determine the location for water or contaminant sampling wells, it is extremely important to use subsurface (downhole) remote sensing methods in addition to surface-based and aerial methods in order to develop reliable information on the vertical dimension. We cannot overemphasize the necessity of at least one "calibration" hole if an accurate and full-information interpretation of subsurface geophysical data is to be made. This effort need not be extensive, that is, one hole may suffice, but our experience has shown that data from surface techniques alone cannot be accurately and confidently interpreted without aid of downhole data. As shown in the examples of simulated subsurface log data in Fig. 3, physical property data, such as resistivity, spontaneous potential, induction and natural gamma radioactivity levels, can provide detailed hydrogeological structure data that can be integrated with already existing well drilling, geologic, hydraulic, and topographic data to provide a much clearer interpretation of data collected with surface sensors. The cost of acquiring downhole data will usually be readily offset by increased confidence in the interpretation of surface-based measurements. Consequently fewer monitor wells will be required to obtain samples or structure data. From the environmental monitoring standpoint, the investment in time and money for surface-based and downhole measurements can greatly improve the likelihood that a subsurface sampling or instrumentation network will detect and monitor movement of contamination from a waste site.

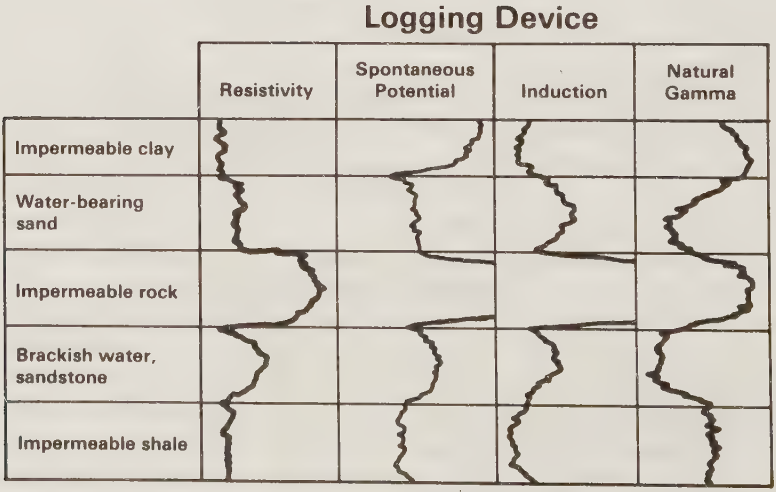

FIG. 3—*Simulated subsurface log data* [8].

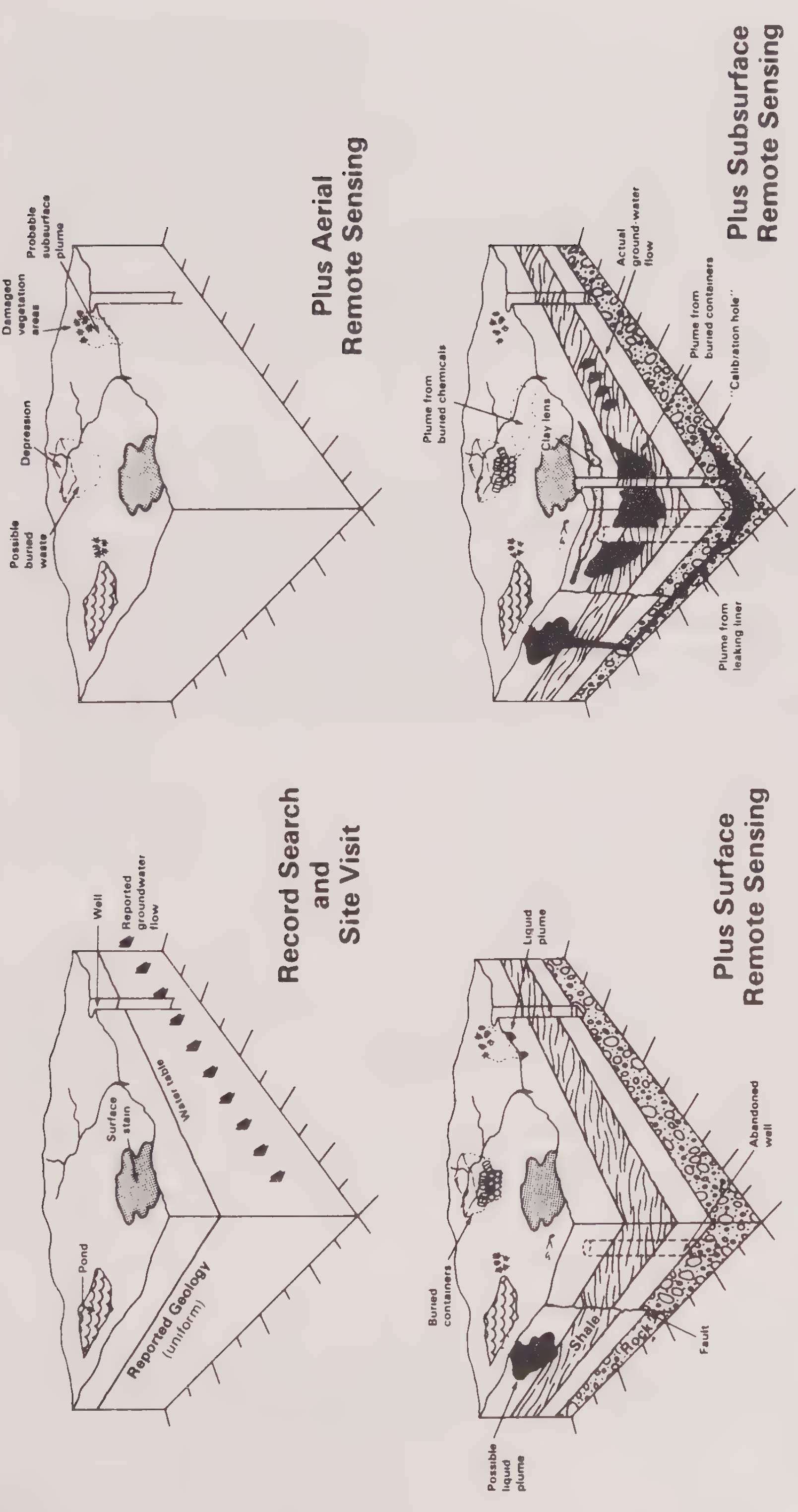

FIG. 4—*Progression level of subsurface information gain using remote sensing.*

The value of adding remote sensing to the suite of investigating practices, and the criticality of including subsurface (downhole) methods, is portrayed in Fig. 4.

As an additional note long-term subsurface monitoring programs may also be made more cost effective (in terms of emplacement costs and operational costs) by employing sensing techniques such as ground-water contaminant detection using laser-induced fluorescence via fiber optic cables. The state of the art has not yet advanced to operational status but is indeed promising [*10*]. At present, effective physical sampling techniques must still be employed for reliable saturated zone and unsaturated zone monitoring [*11*].

Conclusions

We have found that the role of aerial, surface-based, and subsurface remote sensing should not be overlooked for subsurface investigations and monitoring of waste sites, whether the site is being evaluated for use as a waste storage or disposal site or it is a site where waste handling has already occurred. Indeed, a combination of these three techniques is often the most cost-effective and productive in supplying the required information.

Use of remote sensing provides valuable three-dimensional information that can reduce costs by reducing the need for drilling holes to collect subsurface physical structure and chemical composition data. If surface sensing techniques are to be used, supplemental use of subsurface techniques is critical to assure accurate interpretation of surface sensor data. If either surface or subsurface investigations are to be conducted, aerial remote sensing is extremely valuable and may be essential to provide guidance for the investigation. Even then, data misinterpretation can readily occur if operators and interpretors are not adequately experienced and skilled.

Depending on the level of detail of subsurface information required, a three-level hierarchy of the three methods is recommended, each leading to effective design of subsequent levels. As some techniques can provide useful information and others can be useless depending on specific site conditions, guidance should be sought from experience of others before committing to a program. Care must also be taken to assure that the surface and subsurface sensor systems used are appropriate for the relatively shallow depths associated with waste site subsurface investigation, compared to systems in use for much deeper subsurface characterizations associated with petroleum and mineral exploration.

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Waste Testing

Alan R. Rohlik[1]

The Complex Matrix in Environmental Chemistry for the Petrochemical Industry

REFERENCE: Rohlik, A. R., **"The Complex Matrix in Environmental Chemistry for the Petrochemical Industry,"** *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 257–272.

ABSTRACT: This paper presents specific examples of problem solving involving the complex matrix. The purpose is to encourage development and comparison of methods with the goal of creating systematic analytical protocols for many waste types.

Complex matrix chemistry is becoming more important in environmental analysis. Many waste matrices are unique to an industrial process and common worldwide. Only recently has analysis of many complex wastes been attempted, primarily because of environmental concerns and regulations. The complex matrix can be multiphase, chemically unstable, and contain analytical interferences. Complicating factors include waste aging and total versus releasable constituents.

Multiphase wastes can contain organic compounds, water, and solids. Examples of centrifugation and extraction of sludges are shown to simplify analysis. The extracts are more uniform and can be analyzed separately with more reproducible results. However, careful attention must be paid to mass, volume, and specific gravity of the separated fractions to be able to reconstruct the original samples. Anaerobic bacteria in petroleum refinery sludges can rapidly generate sulfide in a sample and lead to misleading conclusions about the real hazard of the waste.

Analysis for sulfide immediately after sampling is recommended. Other changes in chemically active wastes, including oxidation, often occur naturally in the disposal environment. These changes caused by aging are shown to confound analytical results and make interpretation of environmental impact difficult.

Matrix interferences in sulfur analyses can be overcome with appropriate analytical techniques. Matrix effects are explained, and comparisons of X-ray fluorescence and combustion are made. The sulfur result is also shown to present a problem in heat content calculation. The success of total assay of metals is dependent on specimen preparation. A comparison of three methods is given and a recommendation made. New test methods under development by ASTM for environmental modeling are presented as future options. The use of background information is recommended to optimize analytical techniques and provide the most useful data.

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KEY WORDS: industrial wastes, oily wastes, waste preparation, complex waste matrix, oil, inductively coupled plasma spectroscopy (ICP), EPA tests, method comparison, hazard assessment, quality assurance, Resource Conservation and Recovery Act, data interpretation

Interest in complex matrix environmental chemistry increased in the United States with implementation of the Resource Conservation and Recovery Act (RCRA) in 1980. Until that time, many wastes were considered too complex to even attempt the most basic analyses. In some cases, process by-products became wastes merely because they could not be analyzed. The RCRA analysis manual, SW 846, provided the first general approach to samples with unusual matrices. Since 1980, many improvements have been made in this area by government and industry. This paper discusses some of these improvements.

It begins with separation and preparation of specimens, discusses the implication of oxidation and reduction, and considers the adaptation of simple matrix methods. It ends with new opportunities in environmental modeling and the need and use of background information as waste and process analytical tools.

Separation/Preparation

Centrifugation

Wastes, such as drum cleaning sludges, may contain mixtures of water, liquid organics, and particulates. These usually separate incompletely into layers that prevent removing small representative aliquots. Centrifugation in graduated centrifuge tubes will separate the sample into stable layers of measurable volume. Each layer can then be sampled for analysis, for example, total metals or heat content, and density. After each layer is sampled, it is drawn off by vacuum to expose the next layer. After analysis is complete, density and volume measurements are used to reconstruct analytical results for the entire sample. Furthermore the individual layer results may suggest process scale centrifugation to separate especially valuable layers for use as fuel or metals recovery.

Pressure Filtration

This technique is required by the U.S. Environmental Protection Agency (EPA) to separate free liquids from wastes and separate solids from extraction procedure (EP) toxicity leachates [*1*]. Nitrogen gas at 5.3-kg/cm^2 pressure is used to force the liquid portion of a sample through coarse and fine fiberglass filters and then a 0.45-μm membrane filter.

Stable emulsions can be immiscible oil and water phases that are thor-

oughly held together by very small amounts of solids. One cooling tower sludge had only 1.8% solids as an emulsifying agent. Pressure filtration yielded 13.1% reusable oil, 67.4% treatable water, and 19.3% thick sludge. The three resulting specimens were easily prepared for inductively coupled plasma (ICP) metals analysis. The standard techniques used were xylene dilution of the oil, a U.S. EPA acid digestion for water [*2*] and a Sohio-developed solids digestion procedure [*3*]. Pressure filtration alone provided simple matrices to analyze. It also demonstrated a potential large-scale application for oil recovery and an 80% reduction in the mass of waste.

Calculations

The essence of analyzing the unusual matrix is to separate the sample into simpler, more uniform phases. These phases may be water-free organic, liquid-free solid, and suspended solid-free water. Each of these uniform phases can be analyzed by established methods requiring little or no modification. The final step is to reconstruct the original sample from the sum of analytical results of the various phases. This can only be done if detailed volume, density, and mass measurements are made during the separation process.

Analyses are more accurate if conducted on a mass to mass basis, for example, milligrams per kilogram, (mg/kg), rather than mass to volume, for example, milligrams per litre, (mg/L) since sample density may vary. Mass, volume, and density measurements of the original sample and all of the separate phases should be made.

Often the best way to calculate the mass of multiple liquid phases is from volume and density measurements. Density is determined by weighing a specific volume of sample with volumetric pipets or graduated syringes. Calculation of mass is preferred over direct weighing of the entire phase. This is because complete separation of liquid phases of similar polarity and density can be too difficult to perform with certainty. The validity of volume, density, and mass measurements or calculations is established by checking for mass balance. This test of validity on real samples is significant because few standard samples are available to determine the accuracy of the separation procedures. For example, a certain mass of sample is pressure-filtered. The masses of filtered solids plus filtrate should compare to total mass within 3%. The filtrate is composed of a two-phase liquid. The two phases are separately measured for volume and density. The masses of the two phases are added and should equal the mass of the total filtrate within 1%. Note that U.S. EPA has a similar protocol, tentatively identified as Method 1330 in the analytical methods book, SW 846.

Waste disposal data other than leachate are typically required on a total "as-received" basis rather than as data for the individual separated phases. Therefore, it is essential to perform the earlier mass balance calculations to ensure that significant error does not occur because of miscalculation in the

phase separation steps. Data on the individual phases may also be of interest for purposes of waste treatment, volume reduction, process control, process improvement, or resource recovery. In these cases it may be useful to present the separate phase data as well as the calculated total sample data on one table (Table 1).

The values for total sludge analysis with respect to U.S. waste disposal regulations show a potential chromium problem and some concern about the zinc concentration. The data for pressure filtered solids show that volume of waste to be disposed of can be easily reduced by more than 80% and that chromium and zinc are concentrated into the solids phase. The data for filtrate water show that it can be readily accepted by the existing waste water treatment plant. The data for filtrate oil show that it is probably acceptable as refinery feedstock or refinery fuel.

Comparison of Specimen Preparation Methods

A variety of specimen preparation methods for specific analyses is often available. The methods are often general, or designed for a particular matrix,

TABLE 1—*Cooling tower oily side sludge, as received. The sample is a light tan-gray stable emulsion.*

		Observed Values			
Parameter	Units	Total	Filtered Solids	Filtrate Water	Filtrate Oil
Solids, Oil Water	wt%	100	1.8	87	12.2
Pressure Filtration	wt%	100	19.3	67.4	13.1
Silver, Ag	mg/kg	...	...	<0.3	...
Aluminum, Al	"	520[a]	2700	<0.1	<1
Arsenic, As	"	9.8 min	50	<0.3	...
Barium, Ba	"	<6.5	30	0.88	<1
Calcium, Ca	"	1300	6500	85	10
Cadmium, Cd	"	<4.1	20	<0.1	<1
Chromium, Cr	"	680	3500	0.28	8
Iron, Fe	"	770	4000	0.11	4
Mercury, Hg	"	...	...	<0.001	...
Magnesium, Mg	"	38 min	...	56	<1
Manganese, Mn	"	...	...	<0.01	...
Sodium, Na	"	170	300	160	10
Nickel, Ni	"	3.0 min		<0.2	22
Phosphorus, P	"	98	500	...	10
Lead, Pb	"	<6.5	<30	<0.3	4
Selenium, Se	"	...	<30	<0.3	...
Silicon, Si	"	1600	8500	...	1
Tin, Sn	"	2.6 min	...	...	20
Titanium, Ti	"	31 min	160	0.08	<1
Zinc, Zn	"	290	1500	...	2

[a] $520 = (0.193 \times 2700) + (0.674 \times <0.1) + (0.131 \times <1)$.

for example, fuel oil, tar, soil, and so forth, but not necessarily for the waste to be analyzed. These limitations make it difficult to choose the best method to achieve the desired result. Several methods may have to be tried to find the most appropriate ones. Even if calibration standards in the final preparation matrix are adequately recovered, analytically results may still be inconclusive.

Example 1 (see Table 2)—The first judgment of method selection is whether sufficient data can be acquired. In the United States, the U.S. EPA requires data for eight metallic elements in its test for EP toxicity: silver, arsenic, barium, cadmium, chromium, mercury, lead, and selenium (mercury analysis was not conducted on these samples). Other elements may also be of interest. The second question is whether the quantifiable detection limits are low enough to meet requirements. This question is answered yes for all elements in the preparation methods used in this case. The third consideration is whether the method is inherently uncertain for some results. The above questions must be well examined before more qualitative judgments are applied.

An important consideration is the comparison of maximum and minimum results for the same parameter. Even though all quality control results may be acceptable, different preparation methods do produce different results. For example, the quality control (QC) sample matrix may not be similar to the sample matrix. For environmental prudence, it is better to use the highest reasonable analytical result and avoid the lowest. All these judgments are applied to the measurement of 26 metals as shown by Table 2 data. It is clear the xylene dilution and ashing/bombing do not produce data[2] for enough elements of interest. Digestion produces uncertain results for two elements of interest and no results for two more. All the methods have significant limitations. Of the three preparation methods for inductively coupled plasma (ICP), at least two methods will have to be used in any new analysis of heavy oil. One of those methods must be digested because the other two cannot provide cadmium results. Final selection in this case is based on the number of elements with minimum concentration results. Since xylene dilution produces only two minima and ashing/bombing produces nine, xylene dilution becomes the second method of choice. Of the results obtained by the two analy-

[2]Metal's analyses by ICP may not provide data for a variety of reasons. The following are typical examples of less than optimal operating conditions. In xylene dilutions, organically soluble standards may not be readily available or in use at the time of the analysis, for example, arsenic, beryllium, mercury, and selenium. Cadmium was receiving interference from the copper channel but only in organic matrix samples at the time of these analyses. Potassium is a weak element by ICP, and it is also sensitive to organic noise. It would require great effort to quantify considering its trivial addition to our knowledge. Boron and cobalt were difficult to quantify because of noise and were considered unimportant in this case since all data indicated both elements were low in concentration. Ashing/bombing uses boron and magnesium in reagents so these elements cannot be quantified. Potassium is again weak, particularly in a solution of high ionic strength. Tin precipitates in this method. There is no recollection in the lab over why cobalt data were rejected at that time, and the original data are merely "*X*"ed out. Digestion-silicon precipitated, and tin was not part of the standard mix run at that time.

TABLE 2—*Heavy oil analysis by ICP, mg/kg.*

Parameter	RCRA Limits	Xylene [4] Diluted Extract	Ashed/ Bombed [3] Extract	Digested [5] Extract
Ag	5.0	0.2	<0.1	...
Al	...	11	6.1	14
As	5.0	...	1.4	<0.8
B	...	...	...	<0.8
Ba	100	2.4	3	2.2
Be	...	...	<0.01	<0.8
Ca	...	69	150	71
Cd	1.0	...	...	<0.2
Co	...	...	0.37	<0.8
Cr	5.0	0.8	0.66	<0.8
Cu	...	1.5	1.1	3
Fe	...	49	30	69
K	...	...	...	<16
Mg	...	6	...	7
Mn	...	0.8	2.9	0.8
Mo	...	3	0.63	<0.8
Na	...	190	160	40
Ni	...	<6	8.6	<1
P	...	18	6.6	8
Pb	5.0	17	6.4	9
Se	1.0	...	0.32	<0.8
Si	...	2	10	...
Sn	...	3	...	...
Ti	...	0.5	0.40	1.4
V	...	32	19	36
Zn	...	21	11	23
		QUALITY OF RESULTS		
Number elements with results unobtainable or unavailable		8 As, B, Be Cd, Co, Hg K, Se	5 B, Cd, K Mg, Sn	2 Si, Sn
Number of elements showing highest concentration		5	5	6
Number of elements showing lowest concentration		2	9	2
		METHOD LIMITATIONS		
		uncertainty for Na, Ni, Mo because of high background noise from carbon	potential loss of volatile elements in open container digestion; uncertainty for Ag because of possible chloride precipitation	high reagent requirements long digestion time uncertainty for Ba, Pb because of possible sulfate precipitation

ses, significantly higher results are normally reported. Similar results are averaged.

Example 2—The optional criteria of choosing maxima rather than minima sometimes takes precedent over regulation and standard practice. EP toxicity leachates [*1*] are the result of agitating 20 to 1 water to waste mixtures that have been adjusted to pH 5.0 ± 0.2 with 0.5 *N* acetic acid over a 24-h period. The mixture is filtered through a 0.45-μm filter, and then the filtrate is preserved for analysis. Acetic acid and other organics can interfere with some element analyses. As a standard practice in our laboratory, this interference is routinely removed from the leachates, using a U.S. EPA acid digestion procedure [*2*].

This digestion yielded a precipitate only once since 1979 in our laboratory. The digested and undigested leachates were analyzed by ICP to determine what element(s) was precipitated. It was learned that the standard U.S. EPA digestion procedure precipitated molybdenum (molybdenum in leachate = 610 mg/L, molybdenum in digested leachate = 220 mg/L). ICP resolved this question much more easily than atomic absorption would have.

Oxidation/Reduction as Analytical and Interpretation Considerations

It is assumed that chemical oxidation and reduction in waste samples should be minimized before analysis. This ensures that the sample analyzed remains as representative as possible of the waste from which it was taken. This assumption must be questioned on a case by case basis.

Penland et al. [*6*] site the example of metal sludges that are placed in drying beds before disposal. The drying oxidizes and immobilizes the metals as well as reduces the waste volume. Analyzing the sludge when it is placed in the beds would not give a true picture of waste leachability since the drying step reduces leachability by about a half. Analyzing the dried sludge means that the waste must be stored on site until analysis is complete. Drying and therefore oxidizing samples in the laboratory can save time and money by allowing analysis to be completed before the sludge is completely dried in the beds.

Oxidation in the laboratory can be used as an analytical tool as well as a simulation of a process. For example, a black scale in a refinery process unit was suspected to be ferrous sulfide. This had to be confirmed to determine whether feed to the unit was contaminated with reactive sulfide. Confirmation was also important because ferrous sulfide can auto-ignite under some disposal conditions. Iron content was determined easily at about 61% using conventional dissolution and ICP analysis techniques. Sulfur content was not easily determined by our best method at the time, X-ray fluorescence, because of iron interference and a lack of standards. However, the presence of ferrous sulfide could be strongly inferred if ignition of the sample produced rust colored product (iron oxide [Fe_2O_3]) and a theoretical loss on ignition of 9.2 weight percent. The ignition was performed, producing the expected color change and a weight loss of 9.3%.

Releasable Sulfide in Wastes and Waste Samples

Waste containing sulfide that can be released to the environment is considered hazardous in the United States. No widely acceptable test or concentration limit has been established so any detectable presence of sulfide is of concern.

Waste storage and biological waste-water treatment in the refining industry produces biologically active sludges containing some anaerobic sulfur-reducing bacteria. Furthermore, waste analysis, because of the complexity, is often performed off-site, which delays the analysis. That delay allows the anaerobic bacteria to generate sulfide in the sealed sample bottle. Our attention began to focus on the problem in early 1982. Two analytical reports were questioned because sulfide was obvious in our samples but not noticed at all by refinery personnel, sludge handlers, or disposers. The discrepancy was attributed to long transportation times (four to twelve days) and insufficient cooling during transportation. A typical result is less than 0.5-mg/kg sulfide just after sampling and 320-mg/kg sulfide ten days after sampling. This increase in total sulfide concentration during transport can change the classification of a waste from nonhazardous to hazardous. Therefore, it is important to be aware of this and other possible changes that may occur between sampling and analysis. The problem is solved by total sulfide analysis on site immediately after sampling.

Just as sulfide is easily generated in transportation, it is just as easily destroyed during analysis. A transported sludge sample contained more than 5300 mg/kg in releasable sulfides [7] before the U.S. EPA leaching test. Analysis of the highly oxygenated EP toxicity leachate showed a concentration of only 2.8 mg/kg (0.14-mg/L sulfide in the leachate). These results further illustrate that analysis should be run on the fresh sample to be valid.

Aging

Current waste analyses have been shown to be poor predictors of how wastes act in the disposal environment. Part of the problem is due to the lack of consideration given to waste aging. Although no detailed studies have been run, it has been noted in our laboratory that sealed, unpreserved leachates can change color or form precipitates over time. Clear leachates have turned orange within two weeks with as little as 14-mg/L iron concentration. Other leachates containing colored metal ions tend to become clear, sometimes generating a precipitate. This is probably due to slow oxidation. While reduced and soluble metals in fresh wastes will readily leach, insoluble oxides, formed when disposed of in an oxidizing environment, will not. Therefore, typical analyses in these cases could greatly overestimate the leaching potential of the waste.

Acceptability of Simple Matrix Analytical Methods to the Complex Matrix

The analytical coordinator is often requested to provide data on wastes for what seem to be common or simple analyses. It is easy to send the sample to an appropriate laboratory with only an analytical request. However, the laboratory cannot adequately analyze the sample without the help of the coordinator. The complex waste matrix can make even the simplest analyses more difficult.

Total sulfur analysis is often requested for wastes to be destroyed by incineration. The data are used to determine potential sulfur dioxide emissions and as a correction factor in heat content analysis. At present, there are three methods that I prefer to determine total sulfur content in liquids:

- *X-Ray Fluorescence (XRF):* The sample is irradiated with X-rays, which cause sulfur atoms to fluoresce quantitatively. The procedure takes less than five minutes, but requires calibration with similar matrices. Furthermore, many metals, including iron, interfere.
- *Microcoulometry:* The sample is combusted at 800°C. The resultant sulfur dioxide gas is dissolved in a solution and then titrated. This is the most accurate technique. However, only 10 μL of sample are used. Because the sample size is so small, there can be very little sample heterogeneity, or several specimens must be analyzed. The technique also requires great skill by the analyst.
- *Combustion with Infrared Detection:* The sample is combusted at 1370°C, and the resultant sulfur dioxide is measured by infrared absorbance. This method is best suited to solid samples. Analytical precision requires great skill from the operator for specimen preparation and specimen introduction into the furnace.

Table 3 presents some comparative results from analysis of laboratory waste organic liquid storage tanks. Comparison of data for Samples 1 through 4 showed much higher results from XRF than from microcoulometry. Discussion with the analysts about sample types and results established that XRF was probably more reliable in this case. ICP data showed that metal interferences were small in the XRF analysis and combustion was visibly incomplete in the microcoulometry apparatus. Accuracy of the results was not easy to confirm in these matrices, so another comparison between XRF and combustion infrared detection was made. This comparison was much better than the first, though some discrepancies remained. It is possible that some uncombusted organics were measured by infrared (IR) and could account for the discrepancies. XRF became the preferred method because it is reasonably accurate, faster, and much less expensive on a cost per analysis basis. It is clear that more comparative analyses should be run with the goal of identifying matrix types suitable for analysis by each method.

Any analytical method, no matter how common, must be carefully re-

TABLE 3—*Comparative sulfur analyses on waste organic liquids, mg/kg.*

Sample Number	X-Ray Fluorescence	Microcoulometry	Combustion, Infrared Detection
1	11 000	1800	...
2	170	150	...
3	2 300	640	...
3 (duplicate)	2 300	1700	...
4	1 600	400	...
5 (total)	1 940	...	2200
5 (top 60%)	3 000	...	3500
5 (middle 20%)	620	...	500
5 (bottom 20%)	90	...	200
6	350	...	4400
6 (duplicate)	350	...	...
6 (duplicate)	380	...	...
7	3 400	...	3500
7 (duplicate)	3 400	...	3300
8	3 200	...	3200
	STANDARD		
Theory	660	660	
Found	740	760	
% Recovery	112	115	

viewed when applied to the unusual matrix. Incineration is often the method of choice for disposal of petrochemical wastes. Incinerator operators require heat content analysis to ensure a successful burn. ASTM Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (D 240) is commonly used in the petroleum industry. However, it cannot be directly applied to wastes. Because no method is written for this purpose it is necessary to adapt a similar existing one.

The ASTM D 240 calculation for heat content of fuels is

$$H_g \text{ (Btu/lb)} = [1.8 \, (tW - e_1 - e_2 - e_3]/M$$

where

H_g = gross/heat of combustion, Btu/lb;
1 Btu/lb = 1.8 calories/g;
t = change of temperature of water bath in the calorimeter, °C;
W = $(Hm + e_1 + e_3)/t$, which calibrates the calorimeter with a standard,
H (calories/g) = heat of combustion of a benzoic acid standard;
m = mass of benzoic acid used in the calibration, g;

e_1 (calories) = heat of nitric acid formation (determined by titration with 0.0725 N sodium carbonate, (Na_2CO_3). Millilitres used = calories/g;
e_2 (calories) = 14 M^1, which is the heat of formation of sulfuric acid;
14 = heat of reaction/1 g of sulfur for the reaction of $SO_3 + H_2O \rightarrow H_2SO_4$ + heat;
M^1 (g) = mass of sulfur in sample;
e_3 (calories) = H_1m_1, which is the heat of combustion of the firing wire to start the test where H and M, are established for the specific type and length of wire consumed; and
M (g) = mass of sample.

Because waste samples do not always burn without help, the analyst sometimes adds mineral oil to the calorimeter. In turn, this requires a new "e_4" term to be subtracted along with the other "e" terms:

e_4 (calories) = H_2m_2, which is the heat of combustion of mineral oil used to assist sample combustion;
H_2 = 11 000 calories/g; and
m_2 = grams of mineral oil.

Other changes are necessary. There is a problem converting the e_2 calculation for fuel samples to waste samples. The sulfur in fuels is presumed to have a minus two oxidation state and be attached only to carbon or hydrogen or both. Waste samples, on the other hand, may have sulfur in many oxidation states and may be attached to many different elements including oxygen as sulfate. Sulfur in this case does not react as it does in fuels, and the e_2 term is therefore questionable.

There is a similar problem converting the e_1 calculation for fuel samples to waste samples. Sulfur and nitrogen are the primary acid-forming elements in fuels. Carbon as the carbonic acid combustion product is also a minor contributor. Waste samples are far more complex. The initial pH and buffering capacity of the waste may be a substantial interference. Combustion products, such as metal oxides, may exist mainly as basic buffers, a negative interference. Therefore, titration with sodium carbonate may not truly indicate the heat of acid formation. The true e_2 value may in many cases be different than test results indicate.

The final reported test and equation become very different from the original

$$H_g \text{ (Btu/lb)} = [1.8\,(tW - e_3 - e_4)]/M$$

Furthermore each result must be qualified as an approximation because the e_1 and e_2 terms are still relevant. In fact many wastes are reported with the e_1 or e_2 terms or both included. However, since they cannot be easily quantified,

inclusions of e_1 and e_2 are used to indicate a rough range for heat content, not a particular value. The size of the range in these cases is one indication of the uncertainty of the test.

New Opportunities for Environmental Modelling

The U.S. EPA developed the first widely used method for determining the leaching effect of landfill disposal of wastes. The test, EP toxicity [*1*], was intended to model codisposal of municipal and industrial wastes. It quickly became apparent that this universal test could not adequately model the many types of wastes and disposal conditions. The EPA is currently working on at least two new methods. ASTM Committee D-34 on Waste Disposal has also been active. What is particularly attractive in the ASTM approach is that the methods will allow the analyst to change or add different steps. These alternatives in the leaching procedure will allow the analyst to more closely approximate conditions at the disposal site.

ASTM Method for Shake Extraction of Solid Wastes with Water (D 3987) is very similar to EP toxicity. The only substantial difference is that the ASTM method uses distilled water while the EPA method includes an acetic acid addition to pH 5.

Four variations on the ASTM generic leaching test (D 3987) would greatly improve the method's flexibility. The variations are (1) sequential batch extraction; (2) use of different extractant fluids; (3) use of waste/waste or waste/soil mixtures; and (4) use of freeze/thaw cycles to determine effect on wastes.

Column leaching has long been thought to be a superior leaching technique. The Committee D-34 method under development was recently shown to be about as precise and sometimes more precise than previous methods.[3] A few improvements in emphasis of critical details should make this an excellent generic method. When the final column leaching method is validated, variations similar to those for ASTM D 3987 may be added.

New and better analytical tools, such as the above, are always welcomed by the chemist and environmentalist alike. However, in our haste to improve, continuity in ongoing studies may be lost. When the need for a long-term study arises, it is essential that every aspect of it is clearly described in detail. Then, as the project evolves, each change or improvement should be recorded. This careful record keeping allows all of the data to be compared if necessary.

Land treatment of wastes is certainly a case in point. In the petroleum industry, land treatment involves spreading a thin layer of oily waste on a relatively large area of land. This treatment method evaporates the water, biodegrades the organics, and the soil accumulates metals. Land treatment sites typically are used for years, with oily wastes being placed on the site as often

[3]Miner, R. A., Van Maltby, C., and Dell, L. R., in this publication, pp. 375–389.

as possible. To ensure most efficient use of the site, oil, water, cation exchange capacity, and metals content of the soil must be monitored at various depths. During the many years land treatment has been used, site management and analytical chemistry have improved greatly. However, the improvements are not always noted as they occur, making it very difficult to compare early and current data of the land treatment site.

A series of twelve separate analyses, spanning seven years, at a company site reveal this problem. Early reports were very short, with little data on field or analytical methodologies. As later data became available, we ensured that details of the work were included for data comparison. However, we certainly had to use improved management and analytical methods as they became available. Also we had to make changes and additions as regulations became more detailed and restrictive.

As the latest report was written, it was clear that only analyses of near surface soil could be compared to all the previous analyses. Even so, sampling, analytical, and quality control techniques have changed enough to cast doubt on continuity of the study. In fact, the changes have been so significant that comparable data can no longer be generated.

The Use of Background Information

Environmental analyses should not be conducted as completely separate from process analysis. A chemist in environmental analysis can often assist the process and business side. The chemist should learn about the individual plant process as well as the wastes to be tested for a variety of reasons:

1. Many methods are available for the same parameter. Knowledge of the waste and likely constituents can help the analyst choose the best methods.
2. The requesting party often has a definite need in mind when making the request, for example, total phosphorus in a land-treated waste. However, it may be necessary to modify the request to meet the need, for example, phosphorus available for microorganisms. The majority of the work noted in this paper is examples of such modifications.
3. All commercial processes that yield wastes have the potential for malfunction or losses (feedstock, product, catalyst, corrosion, and so forth). Waste analysis can be useful in discovering or understanding these problems. Knowledge of the process and current or potential problems with it can guide the analyst to providing useful process as well as environmental information.

The following are examples of analytical method substitution and comparison, data interpretation, and use of historical information:

1. Environmental analysis under RCRA requires, in part, leaching of wastes and leachate analysis for eight metals. In 1980, atomic absorption (AA) was preferred by the U.S. EPA. We chose ICP multielement analysis

instead, because of efficiency and versatility. One spent catalyst analysis by ICP revealed a leachate cobalt concentration of 320 mg/L. The high cobalt concentration was revealed by the general ICP technique because cobalt concentration is determined as well as the RCRA elements. It would not have been found with AA because cobalt analysis was not specifically requested. This single analysis helped to change the spent catalyst from a waste to a salable metal feedstock. The leaching process even suggested an approach to selective extraction of cobalt. Aluminum had the next highest concentration at 18 mg/L.

2. There are extensive deposits of oil shale in the United States. These deposits may become necessary energy sources in the future. Therefore, various means of oil extraction are always being tested. Process waters are rich in organics and difficult to analyze. Analytical research for these samples is not a primary goal of our lab. Therefore, research techniques are not rigorously applied. We have found that some research is unavoidable for assessment of waste-water treatment requirements and costs. One such assessment involved parallel analyses to validate and confirm method adequacy. Results showed

(a) Total carbon by total organic carbon (TOC) or carbon, hydrogen, nitrogen (CHN) analyzer vary by 8.3% of the mean of the two.

(b) The total sulfur result by combustion and titration of sulfur dioxide is 43% lower than the result obtained from serial dilution analysis by XRF. The combustion/titration result, however, is only slightly higher than the summed sulfur concentrations of only four inorganic sulfur compounds obtained by other method. XRF is preferred because it is likely that much of the total sulfur concentration exists as organic compounds.

(c) Total nitrogen by CHN analyzer and total Kjeldehl nitrogen vary by 0.9% of the mean of the two.

(d) Alkalinity must be redefined for this matrix. Manual and automated titrations gave the identical result of 11 000 mg/L as calcium carbonate ($CaCO_3$). Furthermore, the maximum calculated alkalinity from total inorganic carbon was 57 000 mg/L. However, the calcium and magnesium concentrations by ICP calculate to an alkalinity of only 93 mg/L. Alkalinity must be defined as "acid requirement to achieve a desired pH" since it is clearly not $CaCO_3$.

These results will become the background for future analyses in this laboratory. They improve the quality of the data base and provide a solid foundation for future more detailed studies.

3. A series of environmental tests was ordered as part of a new process evaluation. The requested tests included total suspended and total dissolved solids on oily solid-laden process waters. Some samples were filtered as a part of preservation on site, and all samples were filtered later in the laboratory (Table 4). The equilibrium dissolved solids saturation level is about 560 mg/L with a range of 500 to 750 mg/L. Dissolved solids above that level will tend to

TABLE 4—*Process water analysis, mg/L.*

Sample Point	Total Solids	"As Received" Total Suspended Solids	Precipitate from Site-Filtered Sample	Total Dissolved Solids
1	4 000	3300	...	690
	11 000	4600	5 200	750
	2 300	1700	...	590
2	960	400	...	560
	760	100	100	560
	1 300	650	...	650
3	1 600	1000	...	530
	1 900	450	850	560
4	980	480	...	500
	1 400	435	450	560
	1 100	50	...	610

precipitate, perhaps in process lines. The results gave a clear picture of the potential clogging problem. The ability to interpret data was made possible because process details were known by the analyst.

4. Background information is not always technical. On occasion, historical information is the key to understanding the problem. For example, a petroleum product was analytically characterized by fractional distillation and infrared spectroscopy in an effort to determine the source at a refinery. Results indicated that the product was neither a feedstock, intermediate, or product of the refinery. A retired employee of the refinery was contacted. He recalled that a product with similar characteristics was part of a test refining run 20 or more years ago. This information helped us to complete our determination of the source of the material.

Conclusions

Complex matrix analysis is still new and little understood. Improvements can come from any chemist involved in this work, not only government, research, or academic chemists. This paper is the product of many challenges, resulting in small changes in procedure and approach to problems. The changes were made to merely reduce the uncertainty of data and increase its usefulness. Readers are encouraged to exchange their ideas, since small changes in new fields can provide major insight to all of us.

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NOTE: References from the 14 Sohio internal reports that provide the basis for this paper are available only in abridged forms because of proprietary and confidentiality requirements.

Sidney A. Katz[1] *and Stephen W. Jenniss*[2]

Determination of Some Macronutrients and Micronutrients and Some Toxic Elements in Sewage Sludges from Domestic and Industrial Influents Prior to Land Disposal: I. Development of Methods

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ABSTRACT: Procedures for the determination of some micronutrients and macronutrients and some toxic elements in sewage sludge are reviewed and evaluated. Digestion with nitric acid and hydrogen peroxide prior to measurement by atomic absorption spectroscopy was well suited to the determination of heavy metals in sewage sludge nd compatible with the existing requirements and recommendations of the North American and Western European regulatory agencies. Ignition was found to satisfactorily prepare sewage sludge for the determination of phosphorus by spectrophotometry of the molybdenum blue complex, and extraction with water shows promise for isolating nitrites and nitrates from sewage sludge before their spectrophotometric determinations. The criteria used in evaluating the procedures were speed, simplicity, sensitivity, and selectivity.

KEY WORDS: heavy metals, sewage sludge, plant nutrients, land applications, sewage sludge, toxic elements

In the United States and other industrialized nations, many municipalities are currently faced with serious problems in disposing of increasing amounts

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of sewage sludge by economically and environmentally acceptable means. High population densities and limited land area further complicate the problem of sludge disposal in New Jersey.

The contamination of municipal sewage sludges by industrial pollutants prevents some sewage authorities from disposing of their sludge by traditional landfilling procedures. A number of municipal sewage authorities in New Jersey have considered sludge incineration for disposal coupled to steam generation and energy recovery. Some have been prevented from using this technology by the potential impact of heavy metals in their sludges on air quality standards. In alternative disposal plans, even moderately high concentrations of heavy metals preclude the recycling of sludge by land application for fear of phytotoxicity and the possible contamination of ground and surface water through percolation and runoff, respectively.

Listed in Table 1 is a summary of the average heavy metal concentrations in the sludges from eight New Jersey sewage authorities for the 1980 calendar year. Authorities NJ 1 and NJ 2 received only domestic wastes; the other authorities had substantial industrial contributions to their influents. Although Klein et al. [*1*] and Gurnham et al. [*2*] have identified nonindustrial sources as responsible for significant amounts of these metals in the influents to metropolitan New York and metropolitan Chicago sewage treatment works, the data in Table 1 indicate that industrialization rather than urbanization is the major source of heavy metals in sewage sludge. In terms of zinc equivalent, the United Kingdom standard for land application of sewage sludge [*3–5*], the sludges from the New Jersey authorities receiving mixed domestic-industrial influents are from 2.3 to 7.7 times more phytotoxic than are those from the authorities receiving only domestic wastes. In addition, none of the sludges from the authorities receiving the mixed domestic-industrial influents meet the West German standards for disposal to soils used for agriculture or horticulture [*6*], and all exceed the maximum permissable concentrations of heavy metals in sewage sludges for agricultural use under the Dutch [*7*] and Swiss [*8*] regulatory standards. U.S. regulations [*9*] specifically address cadmium, and some federal recommendations [*10*] have been developed into

TABLE 1—*Concentrations of copper, zinc, chromium, nickel, cadmium, and lead in selected sewage sludges, mg/kg dry weight.*

Authority	Cu	Zn	Cr	Ni	Cd	Pb
NJ 1	775	969	148	12	4	153
NJ 2	1170	1 410	285	15	6	265
NJ 3	1940	2 680	1 210	1130	76	1020
NJ 4	3630	5 920	1 150	842	21	1080
NJ 5	1690	10 400	329	68	97	1330
NJ 6	717	3 420	714	136	60	1510
NJ 7	3040	2 680	676	227	93	802
NJ 8	2750	8 150	17 500	62	63	3250

state regulations or guidelines for other heavy metals. Using federal recommendations, Mumma et al. [*11*] found that only 23% of the sludges from their national survey could be considered suitable for land application. By way of contrast, approximately 85% of the West German sludges meet the regulatory standards of the Federal Republic of Germany (FRG) [*12*]. The regulatory and recommended standards for several industrialized nations are summarized in Table 2.

Both the New Jersey hazardous waste management regulations [*13*] and the regulations [*14*] concerning the New Jersey Pollutant Discharge Elimination System (NJ PDES) apply to sewage sludge generated within or transported into the state. Under the scope of the latter administrative code, the New Jersey Department of Environmental Protection (NJ DEP) is empowered to issue permits for the land application of sewage sludge. Recognizing the need for reliable information in making serious decisions on the best course to follow in utilizing or disposing of sewage sludges, the NJ DEP organized a task force to develop, review, and recommend regulatory compliance monitoring procedures in this ill-defined matrix. The task force, with membership representative of the state and federal regulatory agencies, the regulated communities within the state, and the expertise of the state university, accepted this assignment and divided itself into work groups for addressing the problems associated with the analysis of various environmental pollutants in sludge. The Heavy Metals Work Group of the Sludge Methods Task Force directed its activities to developing procedures for the determination of aluminum, arsenic, barium, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, selenium, silver, sodium, tin, and zinc in addition to total phosphorus, nitrate-nitrogen, and nitrite-nitrogen.

The measurement of heavy metal concentrations in sewage sludges can be accomplished using many methods of elemental analysis. In considering approaches to such measurements on a routine basis, speed and simplicity as well as sensitivity and selectivity are major factors.

Atomic absorption spectrometry (AAS) is frequently used to measure the concentrations of heavy metals in sewage sludges. Several regulatory agencies

TABLE 2—*Regulatory and recommended maximum concentrations of heavy metals in sewage sludges for land applications, mg/kg dry weight.*

Country	Cu	Zn	Cr	Ni	Cd	Hg	Pb
Canada	750	1650	1000	160	10	4	450
Federal Republic of Germany	1200	3000	1200	200	20	25	1200
France	210	750	360	60	5.4	2.7	210
Netherlands	600	2000	500	100	10	10	500
Switzerland	1000	3000	1000	200	30	10	1000
United Kingdom	280	560	1000	70	5	2	1000
United States	1000	2500	1000	200	25	10	1000

[15–18] require, or at least recommend, this technique for compliance monitoring, and many research projects on the biocycling of heavy metals from sewage sludge utilize AAS [19–24]. For most heavy metals in sewage sludge, AAS clearly meets the criteria of simplicity, sensitivity, and selectivity. Compared to some other techniques, however, it is somewhat slow.

Inductively coupled plasma atomic emission spectrometry (ICP-AES), with its broad dynamic range and its capability for simultaneous, multielement measurements, shows promise of becoming very useful for the determination of heavy metals in sewage sludge. Sensitivities of ICP-AES are comparable to those of conventional, flame AAS for most heavy metals. Tyler [25] was able to simultaneously measure aluminum, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, and zinc at a rate much faster than that possible by sequential AAS. Tabatabai and Frankenberg [26] have similarly employed ICP-AES for the determination of arsenic, boron, beryllium, cadmium, cobalt, chromium, copper, iron, lead, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, vanadium, and zinc in sewage sludge, and Clevenger et al. [27] have determined boron, beryllium, cadmium, calcium, chromium, copper, iron, magnesium, manganese, nickel, phosphorus, potassium, sodium, and zinc in sewage sludge by this technique. Schrader and Hein [28] have reported that ICP-AES results compare favorably to those obtained by AAS for 23 elements determined in seven different sewage sludges.

Electroanalytical techniques, anodic stripping voltammetry (ASV) in particular, have also been applied to the determination of heavy metals in sewage sludge. Kinard [29] has simultaneously measured the concentrations of bismuth, cadmium, copper, lead, and zinc in both domestic and industrial effluents by ASV. The results were competitive with those obtained by conventional, flame AAS in terms of precision and accuracy, and superior in terms of sensitivity and detection limits.

Wavelength dispersive X-ray fluorescence spectroscopy (XRF) was used by Rethfeld [30] and by Daniel and Häni [31] for the determination of heavy metals in sewage sludge. In both laboratories, specimen preparations involved only drying, homogenizing, pulverizing, and pelleting. In the former, arsenic, cadmium, copper, chromium, lead, nickel, silver, thallium, tin, and zinc were determined with detection limits of from 1 to 10 mg/kg dry weight. The latter was directed to the determination of aluminum, cadmium, calcium, cobalt, copper, chromium, iron, lead, magnesium, molybdenum, nickel, phosphorus, silicon, and zinc. Of the elements regulated under the Swiss statutes, only mercury could not be determined at the limiting value.

Both instrumental neutron activation analysis (INAA) and instrumental photon activation analysis (IPAA) have been used to investigate the elemental composition of sewage sludges. Using multiple irradiations followed by gamma spectrometry after several decay periods, Ryan et al. [32] have measured the concentrations of 44 major, minor, and trace elements in sewage

sludges. Kim et al. [*33*] have determined 14 heavy metals from a single gamma spectrum using a monostandard of either gold or cobalt. Dams et al. [*34*] have determined 41 elements in sewage sludge using a scheme of two irradiations and measurements after five decay periods, and Mumma et al. [*11*] have measured the concentrations of 26 elements from two gamma spectra recorded at different times after each of two irradiations. Chattopadyay [*35*] and Segebade et al. [*36*] have applied IPAA to the determination of heavy metals in sewage sludge. Respectively, they measured the concentrations of 34 and 27 elements. By combining both INAA and IPAA techniques, Chattopadhyay [*37*] measured the concentrations of 50 elements in sewage sludge. Activation analysis has the advantages of minimum specimen preparation, and excellent sensitivities and multielement capabilities for many elements. Analysis time, however, can be several weeks for low concentrations of long-lived radio-nuclides, and facilities for activation or gamma spectrometry may not be readily available for routine determinations.

Many techniques have been applied to the determination of heavy metals in sewage sludge. Atomic spectroscopy, particularly AAS, appears to be the most frequently used approach to such measurements. Instrumentation is readily available in most laboratories, and several interlaboratory evaluations [*38-41*] have confirmed the reliability of the results obtained by this technique. Having identified AAS as the method for measuring heavy metals in sewage sludge, the work group set out to develop appropriate specimen preparation procedures.

A variety of procedures have been employed to prepare sludge specimens for AAS. Many of these have been reviewed by Katz [*42*]. The work group identified four of these for laboratory evaluation: (1) ignition followed by leaching of the ash with nitric acid, (2) digestion with nitric acid, (3) digestion with nitric acid in high pressure decomposition vessels, and (4) digestion with nitric acid and hydrogen peroxide.

Sludge samples were collected from the primary settling tank and from the first stage digester at the Pennsauken Sewage Authority's (identified as NJ 8 in Table 1) treatment plant in Pennsauken, New Jersey. This facility serves some 40 000 domestic customers and handles 15 million litres (4 million gallons) per day of mixed, 50/50 domestic/industrial, sewage. The solids and ash for these sludges were as shown in Table 3.

Samples of these sludges were dried overnight on shallow trays lined with

TABLE 3—*Solid and ashes for sludges.*

Sludge	Total Solids, %	Ash, %
Primary settling tank	5.2	2.0
First stage digester	10.5	3.1

plastic film in an oven maintained at 60°C. Specimens of the dried sludges were prepared for AAS by the four procedures described in the following sections.

Procedure 1—Ignition

Five 200-mg portions of each of the dried sludges were weighed into zirconium crucibles (#10–15, B-J Enterprises, Inc., Albany, OR, USA) and ignited in a bunsen flame. The charred specimens were then placed in a 450°C furnace for 2 h to complete the ignition. The ignited residues were cooled and leached three times with 5 mL of hot 25% by volume (V/V) redistilled nitric acid in high-purity water. The leachates were filtered through Whatman No. 42 paper into 50-mL volumetric flasks and brought to volume with high-purity water. These solutions were diluted as required for the determination of some heavy metals by conventional flame AAS.

Procedure 2—Nitric Acid Digestion

Five 200-mg portions of each of the dried sludges were weighed into 125-mL Erlenmeyer flasks, treated with 5 mL of redistilled nitric acid, and heated gently until the volume was reduced to approximately 1 mL. The flasks containing the specimens as well as those included as blanks were cooled, treated with 5 mL of redistilled nitric acid, and again heated gently. This process was repeated a total of four times to a point where additional acid produced no apparent changes in the contents of the Erlenmeyer flasks. The contents of the Erlenmeyer flasks were then treated with 5 mL of high-purity water, filtered through Whatman No. 42 paper into 50-mL volumetric flasks and brought to volume with high-purity water. Further dilution of these solutions was made as needed for the AAS measurements.

Procedure 3—Digestion with Nitric Acid in High Pressure Decomposition Vessels

Five 200-mg portions of each of the dried sludges were weighed into the Teflon® cups of the decomposition vessels (No. 4745, Parr Instrument Co., Moline, IL, USA), and each, including blanks, were treated with 2.5 mL of redistilled nitric acid. The vessels were closed and placed in a 100°C oven overnight. On the following morning, the vessels were removed from the oven, allowed to cool to room temperature, and the digested contents were diluted with 5 mL of high-purity water. The diluted contents were filtered through Whatman No. 42 paper into 50-mL volumetric flasks, and brought to volume with high-purity water. Further dilutions of these solutions were made as needed for the AAS measurements.

Procedure 4—Digestion with Nitric Acid and Hydrogen Peroxide

Five 200-mg portions of each of the dried sludges were weighed into 125-mL Erlenmeyer flasks. The flasks containing the sludge specimens and empty flasks serving as blanks were treated with 5 mL of redistilled nitric acid and 5 mL of high-purity water. The contents of the flasks were heated gently until most of the solution evaporated. After cooling, 5 mL more of redistilled nitric acid was added, and the flasks were again heated gently until the volume of solution was reduced to approximately 1 mL. The contents of the flasks were again allowed to cool. They were then treated with 1 mL of redistilled nitric acid, 1 mL of high-purity water, and 2 mL of 30% hydrogen peroxide. The contents of the flasks were again heated gently. The contents of the flasks were alternately heated, cooled, and treated with additional 1-mL increments of peroxide four times. The contents of the flasks were finally treated with 5 mL of high-purity water, filtered into 50-mL volumetric flasks through Whatman No. 42 paper, and brought to volume with high-purity water. These solutions were diluted further for measurements of the heavy metals by AAS.

Results of Procedures 1 Through 4

The concentrations of copper, iron, zinc, chromium, nickel, cadmium, and lead in the solutions prepared by Procedures 1, 2, 3, and 4 were measured by conventional, flame AAS. The atomic absorption spectrometer (Model 360, Perkin-Elmer Corp., Norwalk, CT) was calibrated with standards in nitric acid and operated in accordance with the manufacturer's directions. The results for the concentrations of these seven metals in the primary settling tank sludge are presented in Table 4, and those for the sludge from the first stage digester are listed in Table 5.

It is quite clear from the data in Tables 4 and 5 that the results obtained from the sludges prepared by ignition, Procedure 1, are lower than those obtained from the sludges prepared by the "wet" procedures. Furthermore, it appears that the cadmium and lead results obtained from sludges prepared by nitric acid digestion, Procedure 2, are lower than those obtained from sludges prepared in the decomposition vessels, Method 3, and from sludges prepared by digestion with nitric acid and hydrogen peroxide, Method 4.

Procedures 3 and 4 appeared to give the highest recoveries of copper, iron, zinc, chromium, nickel, cadmium, and lead. The use of the high-pressure decomposition vessel, however, presented some problems. Reports of explosions have brought warnings on their use with nitric acid [*43,44*], and their initial cost, $135.00 each, may not be made up in reduced labor for some time. While more labor intensive, digestion with nitric acid and hydrogen peroxide was recommended to the task force by the work group for the preparation of sewage sludge specimens. In addition to the work group's recommendation, digestion with nitric acid and hydrogen peroxide was proposed

TABLE 4—*Concentrations of some selected metals in primary settling tank sludge, mg/kg ± σ.*

Metals	Method[a]			
	1	2	3	4
Copper	2 580 ± 92	3 120 ± 417	3 400 ± 124	3 400 ± 115
Iron	10 600 ± 656	13 900 ± 426	15 100 ± 2040	14 800 ± 353
Zinc	7 970 ± 85	8 200 ± 186	8 370 ± 316	8 540 ± 201
Chromium	16 400 ± 1550	21 500 ± 575	19 300 ± 650	20 200 ± 865
Nickel	43.5 ± 15.1	90.6 ± 16.7	67.0 ± 8.5	75.9 ± 7.4
Cadmium	61.0 ± 1.8	64.7 ± 2.2	76.7 ± 1.7	74.1 ± 1.3
Lead	2 680 ± 124	2 790 ± 66	3 410 ± 71	3 220 ± 73

[a]See text for methods.

TABLE 5—*Concentrations of some selected metals in first stage digester sludge, mg/kg ± σ.*

Metals	Method[a]			
	1	2	3	4
Copper	2 560 ± 59	2 850 ± 56	2 970 ± 164	2 950 ± 105
Iron	8 850 ± 471	13 000 ± 231	14 800 ± 405	14 200 ± 601
Zinc	8 060 ± 116	8 300 ± 146	8 150 ± 170	8 410 ± 303
Chromium	14 900 ± 1750	18 300 ± 146	16 400 ± 360	17 100 ± 1540
Nickel	50.5 ± 7.0	77.9 ± 9.3	82.7 ± 14.8	81.4 ± 15.3
Cadmium	58.7 ± 1.7	57.7 ± 1.8	66.3 ± 5.9	61.7 ± 6.7
Lead	2 680 ± 101	2 760 ± 51	3 080 ± 110	2 970 ± 122

[a]See text for methods.

and successfully used by Martin et al. [*45*] and by Krischnamurty et al. [*46*] to prepare sewage sludges for AAS, and both the UK DOE [*16*] and the U.S. EPA [*15*] have recommended this procedure for the preparation of sewage sludges before the determination of heavy metals by AAS.

The task force accepted the work group's recommendation and suggested that the procedure be field tested by way of an interlaboratory comparison. Of the 150 industrial, governmental, and commercial laboratories registered with the NJ DEP for NJPDES permit analyses, 16 volunteered to participate in the interlaboratory comparison. Each of the participating laboratories was provided with a specimen of a reference sludge prepared by the U.S. EPA as a quality control material [*47*], report forms and questionnaires, and directions for preparing the sludge before the determination of aluminum, arsenic, barium, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, selenium, silver, sodium, tin, and zinc by AAS and, if possible, by ICP-AES. The specific directions [*15*] for specimen preparation were

> Weigh and transfer to a 125 mL, conical, Phillips' beaker a 1.0 gram portion of the sample which has been dried at 60°C, pulverized, and thoroughly mixed. Add 5 mL of 1 : 1 nitric acid and cover with a watch glass. Heat the sample at 95°C and reflux to near dryness. Allow the sample to cool, add 4 mL of concentrated nitric acid and again reflux to near dryness. After the second reflux step has been completed and the sample has cooled, add 1 mL of 1 : 1 nitric acid and 3 mL of 30% hydrogen peroxide. Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken with the start of effervescence that losses do not occur or that the reaction is not too vigorous. Heat until effervescence subsides and cool the beaker. Continue the addition of 30% hydrogen peroxide in 1 mL increments with warming until the effervescence is minimal or until the general sample appearance is unchanged. Note: Do not add more than a total of 10 mL of the 30% hydrogen peroxide.
>
> If the sample is being prepared for the flame atomization of cadmium, chromium, copper, lead, nickel, and zinc, add 2 mL of 1 : 1 hydrochloric acid, return the covered beaker to the hot plate and reflux for an additional 10 minutes. After cooling, filter through Whatman No. 42 paper and dilute to 50 mL with deionized distilled water. The sample is now ready for AAS.
>
> If the sample is being prepared for furnace atomization of arsenic, cadmium, chromium, copper, lead, nickel, selenium, silver, and zinc, add 1 mL of 1 : 1 nitric acid, return the covered beaker to the hot plate and reflux for an additional 10 minutes. After cooling, filter through Whatman No. 42 paper and dilute to 50 mL with deionized distilled water. To prepare the solution for injection, withdraw an aliquot, add any required reagent or matrix modifier and dilute with deionized distilled water to twice the volume of the aliquot. The sample is now diluted in 1% nitric acid, and it is ready for injection into the furnace.

For both flame and furnace atomization, for the use of the method of standard additions, for the preparation of standards, for potential interferences, for the addition of special reagents or matrix modifiers, and for the recommended instrumental parameters, reference was made to the state [*48*] and federal [*49*] methods manuals. This information has recently been summarized by Katz and Jenniss [*50*].

The participating laboratories were instructed to prepare five replicate portions of the reference sludge and determine the concentrations of as many of

TABLE 6—*Individual mean results of laboratories participating in sludge analysis, mg/kg.*

Metals	Laboratory							
	1	2	3	4	5	6	7	8
Aluminum	4 200	6 720	4 660	3 800	. . .	4 580	7 600	. . .
Arsenic	. . .	0.98	2.21	0.03	. . .	. . .	1.18	. . .
Barium	. . .	8.44	99.3	437	. . .	. . .	466	. . .
Cadmium	. . .	20.8	19.4	18.2	. . .	23.0	17.9	17.8
Calcium	27 000	15 400	15 800	5 900	. . .	15 900	18 500	. . .
Chromium	160	194	209	190	. . .	181	209	181
Copper	1 050	907	963	945	933	913	936	1 030
Iron	17 000	15 900	691	11 400	15 700	11 700	11 300	17 900
Lead	. . .	441	565	563	524	546	387	496
Magnesium	9 340	2 700	3 480	2 590	. . .	1 070	3 110	. . .
Manganese	228	205	209	228	298	211	174	192
Mercury	. . .	13.8	. . .	12.7	. . .	. . .	6.52	. . .
Nickel	200	154	178	157	172	154	92.8	143
Potassium	. . .	354	1 060	776	. . .	. . .	611	. . .
Selenium	. . .	1.33	. . .	0.01	. . .	. . .	1.55	. . .
Silver	. . .	65.0	132	84.4	. . .	41.0	50.3	. . .
Sodium	848	666	2 300	. . .	. . .	. . .	542	. . .
Tin	. . .	. . .	. . .	. . .	. . .	691	18.7	. . .
Zinc	1 440	1 410	50.2	1 060	1 150	1 060	1 150	1 320

Metals	Laboratory							
	9	10	11	12	13	14	15	16
Aluminum	...	...	...	5 790	...	3 150	3 690	4 270
Arsenic	...	...	...	...	...	0.54	...	34.5
Barium	...	491	...	213	...	424	...	615
Cadmium	17.4	15.8	...	19.2	18.7	17.6	16.3	17.9
Calcium	...	...	...	614	8 730	12 800	...	17 200
Chromium	154	204	243	195	173	230	108	144
Copper	...	1 080	...	983	893	954	830	929
Iron	...	16 400	...	15 600	14 100	13 400	13 200	12 600
Lead	532	451	...	565	484	534	418	714
Magnesium	...	...	...	3 810	...	3 250	...	2 780
Manganese	...	189	...	204	223	166	148	183
Mercury	11.6	...	...	8.60	...	8.36	...	...
Nickel	...	172	209	152	164	184	166	180
Potassium	...	...	...	1 100	589	950	...	...
Selenium	...	...	...	...	...	6.34	...	...
Silver	82.7	52.3	...	93.4	50.7	72.9	51.9	62.1
Sodium	...	...	...	946	...	658	...	781
Tin	...	...	...	119	...	152	...	...
Zinc	...	...	1 350	1 230	1 300	1 230	1 030	814

the 19 metals as possible. The participating laboratories were also requested to comment on the procedure. Not every laboratory was able to determine all 19 metals. The results from the 16 laboratories are summarized in Table 6, and the grand means are compared to the reference values in Table 7.

Only 1 of the 16 laboratories completed the heavy metal determinations by both flame AAS and ICP-AES. The results of these determinations are compared in Table 8.

The results summarized in Tables 6 through 8 were obtained from a "second reporting," that is, the participating laboratories were advised of the reference values after their initial reports were received, and they were asked to comment on any gross discrepancies. Several of the laboratories identified computation errors made in preparing their initial reports, and they provided corrected information. The most common errors were failures to consider dilution factors in the calculation of the final results. Although Laboratory 3 did not identify such errors, it appears from the data in Table 6 that a dilution factor of 1:25 was not considered in calculating the concentrations of iron and zinc in the dry sewage sludge. For this reason, the results for iron and zinc reported by Laboratory 3 were excluded from the calculations of the grand means presented in Table 7.

Intralaboratory precision varied from element to element and from labora-

TABLE 7—*Comparison of results from interlaboratory analysis of sewage sludge with reference values, mg/kg dry weight.*

	Interlaboratory Analysis		Reference Values [47]	
Metals	Mean	2σ Range	Mean	2σ Range
Aluminum	4 850	2070 to 7630	4 557.6	2010 to 7110
Arsenic	6.57	0 to 32.0	16.972	0 to 88.9
Barium	441	193 to 689		
Cadmium	18.5	12.6 to 24.4	20.772	2.49 to 39.1
Calcium	15 300	3700 to 26900		
Chromium	183	107 to 259	204.46	115 to 294
Copper	941	689 to 1190	1 095.3	831 to 1360
Iron[a]	14 500	9720 to 19300	15 155	3810 to 28500
Lead	516	350 to 682	518.76	305 to 733
Magnesium	3 620	0 to 8020		
Manganese	197	147 to 247	204.98	172 to 238
Mercury	11.1	5.1 to 17.1	16.315	0 to 36.1
Nickel	165	111 to 219	198.31	164 to 233
Potassium	775	254 to 1300		
Selenium	2.31	0 to 7.25		
Silver	69.4	15.8 to 123	80.583	0 to 203
Sodium	967	0 to 2150		
Tin	245	0 to 857		
Zinc[a]	1 190	818 to 1560	1 323.1	1190 to 1450

[a]Data from Laboratory 3 were omitted from the calculation of the mean and 2σ ranges for iron and zinc; see text.

TABLE 8—*Comparison of results for heavy metals in sewage sludge: AAS versus ICP-AES, mg/kg* ± σ dry weight.

Metals	AAS	ICP-AES
Aluminum	4 270 ± 0.1	4 310 ± 2.9
Arsenic	34.5 ± 0.1	35.9 ± 0.1
Barium	615 ± 0.1	628 ± 0.2
Cadmium	17.9 ± 2.1	19.5 ± 2.3
Calcium	17 200 ± 0.1	18 400 ± 2.4
Chromium	144 ± 34.8	141 ± 33.9
Copper	929 ± 51.5	842 ± 46.6
Iron	12 600 ± 1370	13 900 ± 1500
Lead	714 ± 78.2	653 ± 71.4
Magnesium	2 760 ± 1190	3 670 ± 360
Manganese	183 ± 12.0	180 ± 11.8
Mercury		
Nickel	180 ± 12.5	163 ± 11.3
Potassium		
Selenium		
Silver	62.1 ± 0.1	63.3 ± 0.1
Sodium	781 ± 0.1	883 ± 9.2
Tin		
Zinc	814 ± 145	1 000 ± 177

tory to laboratory. The individual laboratory means, standard deviations, and coefficients of variation for cadmium and zinc are presented in Table 9. In most laboratories, precision for most of the heavy metals was equivalent to a coefficient of variation of from 5 to 15%.

On an interlaboratory basis, the coefficients of variation were less than 20% for eight of the heavy metals and less than 40% for 14 of the heavy metals. The coefficients of variation for the reference values were less than those determined from the interlaboratory data for only three heavy metals: manganese, nickel, and zinc. At the other extreme, the coefficients of variation for the arsenic, selenium, and tin values determined in the course of the interlaboratory evaluation were greater than 100%.

In terms of accuracy, 127 of 145 mean values were within the 2σ limits of the reference values. Approximately half of the values reported for nickel and half of those reported for zinc were below the 2σ limits for the corresponding reference values. Nielsen and Hrudey [*51*] have also used this reference material. They found that all of their nickel results were within the 2σ limits, but 67% of their zinc results were below 1190 mg/kg. Smith [*52*] reported results for nickel, zinc, and some other heavy metals in this material that were in excellent agreement with the reference values. The apparent discrepancies between some of the results obtained for nickel and zinc and the corresponding reference values are unresolved at this time.

The 16 participating laboratories demonstrated acceptable precision and accuracy in the determination of most of the heavy metals in the reference

TABLE 9—*Evaluation of interlaboratory precision for the determination of cadmium and zinc in sewage sludge.*

	Cadmium			Zinc		
Laboratory	Mean	σ	100 σ/m	Mean	σ	100 σ/m
1	. . .	. . .	. . .	1440	49	3.4
2	20.8	1.1	5.3	1410	108	7.7
3	19.4	0.77	4.0	50.2	0.79	1.6
4	18.2	2.9	15.9	1060	39	3.7
5	. . .	. . .	. . .	1150	20	1.7
6	23.0	7.6	33.0	1060	119	11.2
7	17.9	1.1	6.1	1150	27	2.3
8	17.8	1.5	8.4	1320	21	1.6
9	17.4	1.7	9.8	. . .	. . .	. . .
10	15.8	0.33	2.1	. . .	. . .	. . .
11	. . .	. . .	. . .	1350	73	5.4
12	19.2	1.2	6.3	1230	35	2.8
13	18.7	0.97	5.2	1300	81	6.2
14	17.6	0.48	2.7	1230	42	3.4
15	16.3	2.2	13.5	1030	74	7.2
16	17.9	2.1	11.7	814	145	17.8

sewage sludge material. This reflects both the competency of the laboratories and the efficiency of the nitric acid-hydrogen peroxide digestion procedure used to prepare the specimens. The participating laboratories had little prior experience with this procedure. Most had previously employed either a nitric acid or an aqua regia digestion to prepare sewage sludge specimens for AAS. Five of the laboratories found the nitric acid-hydrogen peroxide digestion procedure to be more time consuming than the in-house procedures normally used, and eight of the laboratories expressed a preference for the nitric acid-hydrogen peroxide digestion procedure. Despite the apparent negative bias in the nickel and zinc results, the nitric acid-hydrogen peroxide digestion procedure appears to be well suited to the preparation of sewage sludge samples before the determination of their heavy metal contents by AAS.

The determination of phosphorus in sewage sludge has frequently been carried out by spectrophotometry of the "molybdenum-blue" complex. Specimens have been prepared by ignition procedures, acid digestion procedures, and procedures involving the extraction of phosphorus from sewage sludge with a wide variety of agents. Representative of these procedures are the ignition procedure recommended by Environment Canada for total phosphorus in sediments [*17*], the acid—persulfate digestion procedure recommended by the U.S. EPA for total phosphorus in bottom material [*47*], and the carbonate extraction procedure recommended by EPA Victoria for available phosphorus in polluted soils [*18*]. These three procedures were compared in terms of phosphorus recovery from the reference sludge prepared by the U.S. EPA

[47]. Phosphorus recoveries were evaluated by both spectrometric and radiometric techniques.

The reference sludge was spiked by suspending 10 g of it in 100 mL of water containing 100 μCi of ^{32}P as disodium monohydrogen phosphate (Na_2HPO_4). The suspension was stirred overnight at room temperature to equilibrate the spike. The suspension was then poured into a shallow tray lined with plastic film, and the spiked sewage sludge was allowed to air dry at room temperature over a weekend. The dried, spiked sludge was crushed and mixed, and fifty 200-mg samples were weighed into Lusteroid® tubes.

Measurements of radioactivity on 25 of the samples were made with a Geiger-Müller counter fixed into a special sample holder. The mean specific activity and its standard deviation were 294 $\pm$ 22°C/min/mg. On the basis of these results, it appears that the sewage sludge was uniformly spiked with ^{32}P. Replicate specimens of the spiked reference sludge were then prepared for evaluating phosphorus recoveries by radioassay and spectrophotometry using the three procedures described in the following sections.

Procedure 1—Ignition

Five 200-mg portions of the spiked sludge were transferred to porcelain crucibles and placed in a muffle furnace at ambient temperature. The furnace was brought to a temperature of 550°C, and the samples were ignited at this temperature for 90 min. After this time, the crucibles were cooled, the ashes were transferred to 125-mL Erlenmeyer flasks, and 30 mL of 1 *N* hydrochloric acid was added to each flask. The flasks and their contents were shaken overnight at room temperature, and the contents were then centrifuged for 5 min at 2000 rpm. The supernates were decanted into 100-mL volumetric flasks and brought to volume with high-purity water.

Procedure 2—Digestion with Acid Persulfate

Five 200-mg portions of the spiked sludge were transferred to 100 mL beakers and treated with 50 mL of high-purity water. One mL of 11 *N* sulfuric acid and 0.5 g of ammonium persulfate were added, and the contents of the beakers were heated on a hot plate until their volumes were reduced to approximately 10 mL. The contents of the beakers were diluted with 50 mL of high-purity water, allowed to cool, and filtered through Whatman No. 42 paper into 100-mL volumetric flasks. The contents of the flasks were brought to volume with high-purity water.

Procedure 3—Extraction with Carbonate Solution

Five 200-mg portions of the spiked sludge were transferred to 125-mL Erlenmeyer flasks and treated with 60 mL of extracting solution made by dis-

solving 42 g of sodium bicarbonate and 1 g of sodium hydroxide in 1 L of high-purity water. The sludge was shaken with the extracting solution for 30 min at room temperature. The suspensions were centrifuged for 5 min at 2000 rpm, and the supernates were decanted into 100-mL volumetric flasks. The contents of the volumetric flasks were brought to volume with high-purity water.

The efficiencies of the three specimen preparation procedures were evaluated on the basis of recovered radioactivity. Reference standards were prepared by diluting aliquots of the original $^{32}P - Na_2HPO_4$ solution used to spike the sludge to 100 mL. Five millilitre portions of these reference standards and 5-mL aliquots of the solutions obtained from the ignition, digestion, and extraction procedures were pipetted into Lusteroid tubes, and their activities were measured with the same Geiger-Müller system used to evaluate the uniformity of the spiking. The results were as follows:

- Ignition procedure: 100 ± 7.2% recovery
- Digestion procedure: 92.1 ± 8.2% recovery
- Extraction procedure: 42.1 ± 2.9% recovery

It appears that the carbonate extraction, Procedure 3, is grossly inferior to specimen preparation by ignition, Procedure 1, and digestion, Procedure 2, in terms of $^{32}P - Na_2HPO_4$ recovery.

The efficiencies of the three specimen preparation procedures were also evaluated by spectrophotometric phosphorus determinations. One- and 5-mL aliquots of the solutions obtained from the ignition, digestion, and extraction procedures were pipetted into 100-mL volumetric flasks. Similarly, 0.0-, 2.0-, 4.0-, 6.0-, 8.0-, and 10.0-mL aliquots of a 10-μg P/mL potassium dihydrogen phosphate (KH_2PO_4) standard solution were pipetted into 100-mL volumetric flasks. The contents of each were diluted to 50 mL with high-purity water, and treated with 1 mL of 11 *N* sulfuric acid and 0.4 g of ammonium persulfate. The contents of the flasks were heated to boiling for 30 min and then allowed to cool to room temperature. Five millilitres of 5% sodium bisulfite in 1 *N* sulfuric acid was added to each flask, and the contents were incubated in a 95°C water bath for 30 min. To each flask, specimens and standards, 4 mL of molybdate reagent prepared by dissolving 8 g of ammonium molybdate and 0.2 g of tarter emetic in 1 L of high purity water were added. The contents of the flasks were mixed, treated with 2 mL of 6% ascorbic acid, and mixed again. The contents of the flasks were brought to volume with high-purity water, and their absorbances were measured at 650 nm in 1-cm cells 5 min later. The results of these measurements are compared to the reference values in Table 10. The results again reflect the inferiority of the extraction procedure. The results obtained with specimens prepared by ignition and digestion were well within the 2σ limits of the reference values.

The work group recommended to the task force the adoption of the ignition procedure, Procedure 1, for the preparation of sewage sludge samples before

TABLE 10—*Results of spectrophotometric phosphorus determinations in a reference prepared by three different procedures, mg/kg ± σ dry weight.*

Procedures	$m \pm \sigma$	2σ Limits
Reference value	11 573	7 500 to 15 600
Ignition procedure	11 300 ± 178	10 900 to 11 700
Digestion procedure	9 400 ± 248	8 800 to 10 000
Extraction procedure	3 270 ± 293	2 800 to 4 300

the spectrophotometric determination of phosphorus. The task force accepted this recommendation with the suggestion that the procedure be field tested in an interlaboratory comparison using the ash obtained from the determination of volatile solids in sewage sludge, method DEP 014 [*53*]. The interlaboratory comparison will be initiated shortly.

The determination of total Kjedahl nitrogen (TKN) in sewage sludge has been successful with the methods currently recommended or required by the Australian and U.S. regulatory agencies [*18,49*]. A variety of extraction procedures have been used to prepare sewage sludge specimens for the determination of ammonia nitrogen, nitrite nitrogen, and nitrate nitrogen. The U.S. EPA recommends distillation procedure 350.2 [*47,49*], and EPA Victoria [*18*] employs extraction with 2 *M* potassium chloride to prepare sludges, sediments, and soils for the determination of ammonia nitrogen. Extraction with 2 *M* potassium chloride is also used by the latter agency [*18*] to prepare specimens for the determination of nitrite nitrogen and nitrate nitrogen. David and Struchtemeyer [*54*] have used extraction with 2 *M* potassium chloride to prepare specimens for the determination of ammonia nitrogen and nitrate nitrogen by ion selective electrode potentiometry. Fiskell et al. [*55*] prepared their samples by extraction with water before nitrate determinations with the ion selective electrode.

In addition to ion selective electrode potentiometry, spectrophotometry has been employed to measure the concentrations of nitrate in the extraction solutions. Spectrophotometric procedures are also applicable to the measurement of nitrite concentrations. Brucine [*49*] and chromotropic acid [*18*] are frequently used as chromophores in the determination of nitrate, and sulfanilamide [*19,49*] or arsenilic acid [*56*] has been used for diazo coupling reactions with naphtylethylenediamine for the determination of nitrite or, after reduction with cadmium, for the determination of nitrate.

Spiked and unspiked samples of the reference sludge are currently being used to evaluate the various extraction procedures and measurement techniques for the determination of nitrite nitrogen and nitrate nitrogen. On the basis of preliminary studies, hot water extraction followed by spectrophotometry of the arsenilic acid-nitrite-naphthylethylenediamine chromogen shows promise for the determination of nitrite nitrogen in sewage sludge. With cad-

mium reduction, it may be possible to determine both nitrite nitrogen and nitrate nitrogen. This possibility is currently under investigation.

To some, sewage sludge is a bothersome waste; to others, it is a valuable resource. Regardless of the perspective, reliable information on its composition is essential for making administrative decisions on the best course to follow in the utilization or disposal of sewage sludge. Such information is available from the laboratory data obtained with the procedures described in the preceding sections.

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Waste Treatment Alternatives

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Waste Immobilization in Cement-Based Grouts

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ABSTRACT: This paper shows that immobilization of industrial and hazardous wastes in cement-based grouts is technically feasible and offers an improved method of waste disposal. Experiments were performed on four simulated waste streams immobilized in cement-based grouts: (1) fly ash; (2) spent limestone scrubber solids; (3) pickling liquor and recovery sludge containing arsenic, cadmium, chromium, copper, manganese, and lead; and (4) a vacuum pump oil containing polychlorinated biphenols (PCBs), Lindane (hexachlorocyclohexane), pentachlorophenol, and 9-9′-dichlorofluorene. The classes of organic compounds represented by this fourth waste are (1) PCB, chlorinated cyclohexane, chlorinated phenol, and PNA, respectively. Leach tests were performed with a simulated ground water typical of aquifers found in Maryville limestone.

KEY WORDS: waste immobilization, cement-based grouts, arsenic, cadmium, chromium, copper, mercury, manganese, lead, selenium, polychlorinated biphenols (PCBs)

Cement-based materials are the most widely used hosts for the immobilization of radioactive low-level waste (LLW) streams because (1) the cost of the materials is low; (2) the processes run at low temperature, use standard "off-the-shelf" equipment, and are adaptable to a wide variety of disposal scenarios; (3) the resulting waste forms are highly resistant to chemical, biological, thermal, and radiation degradation; and (4) high waste loadings are achieved with a minimum waste volume increase when the waste host formulas are tailored to the specific waste streams. Waste disposal programs at four of the U.S. Department of Energy (DOE) sites have demonstrated the applicability of cement-based processes to the disposal of wastes in deep shale formations, shallow-land trenches, and 208-L drums (for subsequent disposal in

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deep geologic repository). The properties of cement-based materials that make them excellent hosts for radioactive wastes also make them desirable for the disposal of hazardous and industrial wastes. The results presented in this paper confirm the technical feasibility of immobilizing these types of wastes with cement-based materials.

Background

DOE Disposal Operations

Wastes immobilized at DOE sites contain salts similar to those found in industrial wastes, such as nitrate, sulfate, phosphate, and fluoride. Therefore, the disposal methods used at the DOE sites, which are described below, are applicable to industrial wastes as well.

Oak Ridge National Laboratory (ORNL) Hydrofracture Grout—The hydrofracture process [*1*] has been used at ORNL for the permanent disposal of pumpable LLW liquids and slurries that are generated in this laboratory's diverse research, pilot-scale demonstration, reactor operation, and isotope production facilities. In this process (Fig. 1), the fluid wastes are mixed with a blend of portland cement, ASTM Class F fly ash, and natural clay minerals to form a pumpable grout slurry that is then injected into an impermeable shale formation at a depth of 200 to 300 m. This fluid grout is forced between the bedding planes of the Conasauga shale where it solidifies in thin grout sheets.

The process has been used at ORNL for over 20 years to dispose of over 18 million L of waste grout [*2,3*]. The development of grouts for the hydrofracture process has formed the technological basis for many applications of bulk in-situ solidification processes. In addition, the operational history of this ORNL disposal technique has established:

(1) the reliability and the recoverability of such large-scale grouting systems from process upsets,

(2) the proven cost of materials, operation, and capital equipment that are lower than most current waste disposal technologies,

(3) the flexibility of grouting systems to accommodate a broad spectrum of waste chemistries with a few simple dry-solid blends, and

(4) the completion of nearly two decades of environmental exposure showing no significant interaction between the host rock and waste form.

Hanford Transportable Grout Facility—The Hanford Transportable Grout Facility (TGF) is managed by Rockwell Hanford Operations, with technical assistance from Battelle Pacific Northwest Laboratory (PNL) and grouting technology transferred from ORNL. Grouting disposal operations are planned to begin in 1986 [*4*]. A key feature of this facility is that it is transportable and can be moved to existing tank farms where waste has been accumulating for 40 years. The grout resulting from combining these wastes

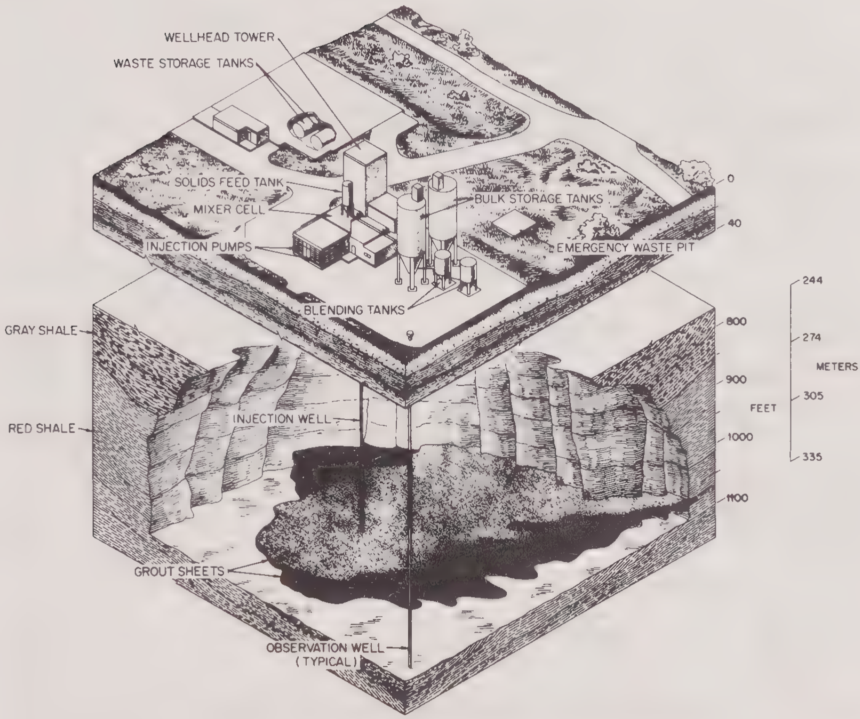

FIG. 1—*Oak Ridge National Laboratory hydrofracture process.*

with cement-based materials will be pumped for permanent disposal in near-surface vaults (Fig. 2).

Savannah River Plant Nitrate Saltstone—During the 25-year operating history of the Savannah River Plant (SRP), process wastes have accumulated and have been stored in double-wall steel tanks. The SRP intends to remove these wastes, separate the radioactive components, and send the resulting high-level defense wastes to the Waste Isolation Pilot Plant (WIPP) in New Mexico for deep geologic disposal. The bulk of the remaining waste is a salt cake composed predominately of sodium nitrate and nitrite. The principal environmental hazard from this waste is the nitrate anion, which forms very soluble salts.

Since 1979, the Savannah River Laboratory (SRL) has been developing a process to safely dispose of the SRP nitrate/nitrite salt waste. In this process, these salt slurries will be mixed with a specially formulated cement-based blend to form a pumpable salt, cement-based slurry that will be solidified in shallow trenches and capped. The goal of this process is to meet federal drinking water standards for nitrate in the nearest groundwater at the upper aquifer's exit from the disposal site boundary.

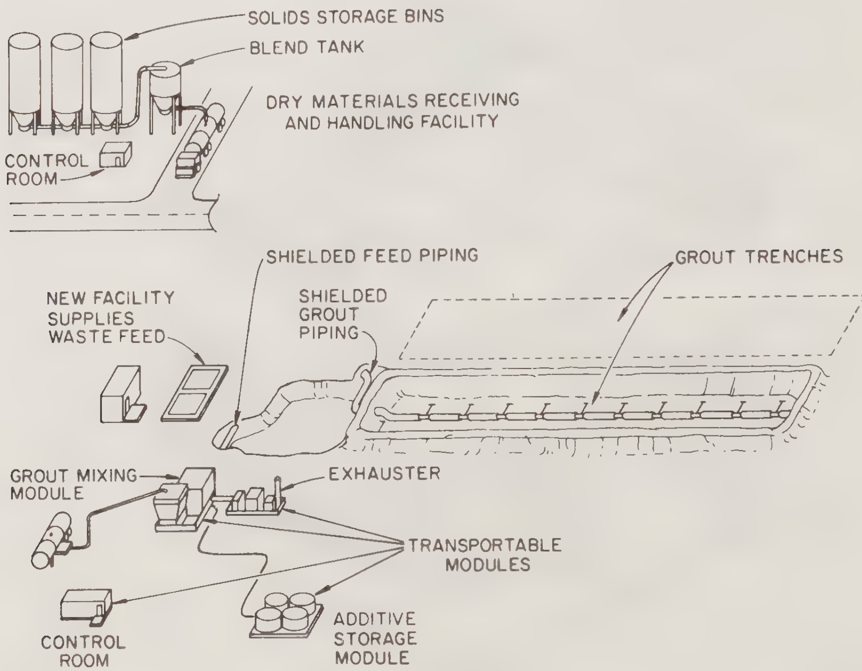

FIG. 2—*Rockwell Hanford transportable grout facility (TGF).*

EG&G Idaho Process Experimental Pilot Plant (PREPP)—Since 1970, transuranic-contaminated (TRU) wastes have been placed in interim storage at the Idaho National Engineering Laboratory (INEL), and about 2800 m^3 of waste is received each year. The final destination of these TRU-waste packages is the WIPP deep geological repository for defense wastes in New Mexico. Because of the waste package degradation during storage and changes in both the WIPP acceptance criteria and regulations governing transportation during this operational period, many of the currently stored packages will be repackaged after their retrieval from the interim storage facilities.

Those packages determined unsuitable for transport to the WIPP facility will first be sent to the PREPP (Fig. 3). All of the unsuitable packages and their waste will be shredded and incinerated to produce a mixture of metals, glass, ceramics, calcined sludges, and ash [5]. This incinerated mix will be screened to separate the fine and coarse fractions. The fine fraction will be mixed with cement [6] and other additives to form fluid grouts [7] that will be poured over the coarse debris in the drums. The grout will then flow into the interstices, encapsulating and fixing both the PREPP coarse and fine wastes into durable monoliths [8]. After a minimum curing time, the cement-based waste form will be transferred to an intermediate storage area, where it will

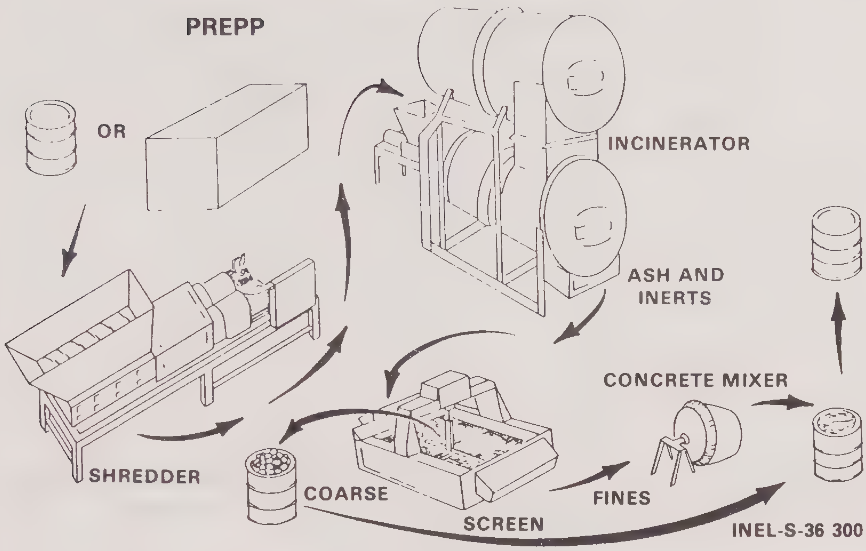

FIG. 3—*Process Experimental Pilot Plant (PREPP) flow diagram.*

remain for 5 to 10 years before being shipped to the WIPP facility for permanent disposal.

Application to Industrial Hazardous Wastes

The preceding section illustrated that cement-based grouts containing waste can be tailored to be compatible with the three major disposal schemes:

(1) disposal in a deep geologic medium, considered by many to be the most environmentally safe disposal scheme [*9*];
(2) disposal in trenches, the most common disposal scheme; and
(3) disposal by packaging in 208-L drums for disposal of small-volume specialty waste.

In addition, the process can be designed to be portable, allowing its application at several industrial plant sites. However, two key questions in the immobilization of industrial waste are (1) can waste be combined with cement-based materials to form a monolith and (2) will the resulting monolith sufficiently retard the release of contaminants upon contact with ground water so as to pose no hazard to the environment? To address these concerns, four simulated hazardous waste streams containing heavy metals and organics were incorporated into cement-based grouts, solidified, and leached with a simulated local ground water typical of acquifers found in Maryville lime-

TABLE 1—*Composition of synthetic ground-water leachant.*

Element	Elemental Concentration, mg/L	Salt	Salt Concentration, mg/L
Ca	5.1	$CaCl_2 \cdot 2H_2O$	18.6
Ba	0.13	$BaCl_2 \cdot 2H_2O$	0.2
K	1.5	KCl	2.9
Mg	1.12	$MgCl_2 \cdot 6H_2O$	9.4
Na	83	from all salts of sodium	from all salts of sodium
Cl	13	from above chloride salts	from above chloride salts
SO_4	7.4	Na_2SO_4	11
CO_3	200	$NaHCO_3$	280

stone (Table 1). The amounts of these heavy metals and organics were equal to, or greater than, those found normally in industrial waste streams.

Experimental Procedure

Waste Stream Simulation

Four simulated hazardous waste streams were tested:

- three containing As (V), Cd (II), Cr (III), Cu (II), Hg (II), Mn (II), Pb (II), and Se (IV); (1) fly ash, (2) spent limestone scrubber solids, and (3) pickling liquor/acid recovery sludge, and
- one contaminated oil waste stream; (4) a vacuum pump oil contaminated with PCBs, Lindane, pentachlorophenol, and 9,9′-dichlorofluorene.

Two batches of each of the four waste streams were prepared. A "blank" contained the waste stream matrix, and a "spiked" contained the matrix and the hazardous constituents. The blank was used as a reference to qualitatively determine if the waste composition or particle size distribution impacts the mixing characteristics of the grout.

Heavy Metal Waste Streams Preparation—All three of the spiked heavy metal waste streams contained similar ratios (by weight) of these heavy metals and the matrix elements. These eight heavy metals are the ones most commonly found in industrial heavy metal waste streams.

The simulated toxic fly ash was prepared by mixing a 50/50% by weight mixture of Kinston fly ash (ASTM Class F) with a blank and spiked oxide stock (Table 2). The blank simulated the major element composition of the Kingston fly ash. These mixtures were also used to prepare the spent limestone scrubber solids (Table 3).

The stimulated pickling liquor waste has 30% by weight chlorides and hydroxides. The matrix and heavy metal chlorides were dissolved in deionized water, the pH was adjusted to about 11 with 30% by weight sodium hydrox-

TABLE 2—*Metal oxide powder composition, ppm.*

Element	Blank	Spiked
Fe	300 000	141 430
Ca	300 000	141 380
Al	30 000	14 100
Mg	30 000	14 240
Na	30 000	14 120
Cr	...	120 000
Cu	...	40 000
As	...	12 000
Se	...	8 400
Pb	...	120 000
Cd	...	20 000
Mn	...	40 000
Hg	...	20 000

TABLE 3—*Simulated spent limestone scrubber solids composition.*

Compound	Amount, wt %
$CaSO_3 \cdot {}^1/_2H_2O$	25
$CaSO_4 \cdot 2H_2O$	25
$CaCO_3$	10
Fly ash waste	40

ide, and the solution stirred for 24 h at 50 to 80°C in order to promote the growth of precipitates. This procedure simulates the aging of the pickling liquor sludge. The compositions of the blank and spiked simulated pickling liquor sludges are shown in Table 4.

Toxic Organic Contaminated Oil Preparation—The simulated oil waste stream was a vacuum pump oil with three polychlorinated biphenol (PCB) isomers, Lindane (hexachlorocyclohexane), pentachlorophenol, and 9,9′-dichlorofluorene (a PNA). These organics, which represent classes of toxic organic compounds (PCBs, chlorinated cyclohexane, chlorinated phenol, and PNA, respectively), were dissolved in a small amount of benzene, mixed with the pump oil, and then gently heated in a 50°C vacuum oven to drive off the benzene. Table 5 gives the concentration of these organics in the oil. The blank oil was this clean vacuum pump oil.

Results

Grout Formulation

The effect of the blank oxides on grout mixability was determined by preparing a grout with only Kingston fly ash without the blank oxides. The same

TABLE 4—*Simulated pickling liquor sludge composition. ppm.*

Element	Blank	Spiked
Al	9 800	2 000
Ca	9 000	3 200
Fe	80 000	27 000
Mg	8 700	3 200
Na	71 000	84 000
As	. . .	3 310
Cd	. . .	4 000
Cr	. . .	2 300
Cu	. . .	5 800
Hg	. . .	3 500
Mn	. . .	7 100
Pb	. . .	20 000
Se	. . .	3 400
Chloride	8.5%	4.77%

TABLE 5—*Toxic organic concentrations in pump oil.*

Compound	Concentration, ppm
2,3,4,5-tetrachlorobiphenyl	1 740
2,2′,4,4′,6,6′-hexachlorobiphenyl	350
2,2′,3,3′,4,4′,5,5′-octachlorobiphenyl	140
Total PCB	2 230
Lindane (hexachlorocyclohexane)	17 400
Pentachlorophenol	17 400
9,9′-dichlorofluorene (PNA)	17 400

amounts of dry-solids and water were then used to make grouts, substituting the blank and spiked fly ash waste streams for the pure Kingston fly ash. The blank fly ash waste stream resulted in a stiffer mix than a similar mix containing just fly ash (no blank oxides). However, the use of the spiked fly ash waste stream in the same mix resulted in a grout that is much less water demanding than the blank oxide mix. This development is a positive characteristic and allows mixable grouts to be made with higher waste loadings and results in higher quality grouts.

The limestone scrubber grouts were the most difficult to formulate because of the large amounts of sulfate, sulfite, and carbonate in the waste stream. These compounds result in highly water-demanding grouts. However, a water reducer/set regulator effectively reduces the water demand to a reasonable level. Again, the presence of the heavy metals in the spiked waste stream resulted in a less water-demanding grout. In the blank limestone scrubber solids grout, these blanks expanded 5 to 10% by volume upon curing. This ex-

pansion was probably caused by the formation of ettringite (a cement hydration product), which is well known for its expansive properties in cement-based grouts. In the spiked scrubber grout, almost no expansion was noted.

The pickling liquor grouts required a suspending agent to prevent the water-rich sludge/grout from separating. The initial grout was very fluid, but it set well with almost no bleed water. The spiked waste stream required slightly more suspending agent than the blank waste stream, further evidence that the heavy metals reduce the water demand. Although the same grout composition was used for both the spiked and blank oils (Table 5), the spiked grout was slightly stiffer (higher gel strength) than the blank grout immediately after mixing.

A summary of the grout compositions used in the leach studies is shown in Table 6. All grouts were cured for 90 days at 100% relative humidity before leaching.

Leach Tests

The solidified grout specimens were subjected to a modified Materials Characterization Center MCC-1 leach test [*10*] using the simulated local ground water as the leachant. The MCC-1 is a static leach test and is designed to quantify the approach of the leachate concentration towards saturation. The concentration at saturation is the maximum concentration achievable in the leachate that is in direct contact with the grout. As such, it provides a reasonable source term for ground-water transport models. In the studies presented in this paper, right circular cylindrical grout specimens with 2.5 cm diameter and 4.5 cm length were leached in 451 mL of simulated local ground water (Table 1). The resulting leachate compositions were determined at 3-,

TABLE 6—*Grout compositions and waste loadings, wt %.*

Grout Components	Fly Ash	Spent Scrubber Solids	Pickle Liquor Sludge	Toxic Organic Oil
Portland cement Type I	20	20	20	19
ASTM fly ash Class F	. . .	. . .	5 to 6.5[b]	17.5
Waste	50	50	67	20
Water	30	30	. . .	37.7
Plasticizer	0 to 0.5[a]	0.3 to 1[a]	. . .	. . .
Attagel 150	. . .	. . .	6.5 to 8[b]	3.3
Microcel E	. . .	. . .	. . .	1.7
Span 80 emulsifier	. . .	. . .	. . .	0.1
Tributyl PO_4 antifoam	. . .	. . .	. . .	0.02

[a]Plasticizer concentrations for the blank and spiked grouts, respectively.
[b]Ranges are for the spiked and blank streams, respectively.

7-, 14-, 28-, and successive 28-day intervals. Saturation was taken to be the leachate composition at interval *N*, which showed no discernable change at interval $N + 1$.

Because the leachates were immediately stabilized with nitric acid to prevent precipitation and to digest any particlates that may have "plated-out" on the leach vessel walls, the pH was not measured. However, these grout formulas were designed with excess silica in the form of fly ash or Microcel E (Table 6). Therefore, any excess calcium hydroxide [$Ca(OH)_2$] will react with the silica to form insoluble calcium hydrosilicates (C-S-H) with a considerable capacity to immobilize heavy metals and to reduce the permeability of the grout matrix. The resulting pH of the grout pore water will be in the range of 9.0 to 10. However, the metal hydroxides to not generally form independent phases, rather they are either coprecipitated with the transitory portlandite [$Ca(OH)_2$] or trapped in the amorphous C-S-H phase(s) forming approximately $Ca(MO_2)_2(SiO_3)_2(OH)_2 \cdot H_2O$. The pH of the simulated high carbonate ground water (~ 200 ppm) is buffered at 8.3 by the carbonate/bicarbonate couple. Consequently, the partitioning of the metals between the leachate and these phases generally results in leachate concentrations that are orders of magnitude lower than the metals' hydroxide solubility constants.

Heavy Metal Waste—Each of the three waste types containing heavy metals and the blanks were analyzed for both matrix and hazardous elements. The major cement matrix elements are aluminum, calcium, iron, and silicate; the minor are magnesium and sodium. Four of the heavy metals, silver, mercury, lead, and silicate, were measured by flame atomic absorption, and all other elements were detected using inductively coupled plasma spectrometry (ICP).

The leach data showed that most of the elements had reached apparent saturation within 28 days. Thus, the 28-day MCC-1 leach data shown in Table 7 represent the maximum concentration of ground water in contact with the grout monolith containing spiked waste. The lowest heavy metal concentrations occur for the fly ash waste stream, the highest, for the pickling liquor waste stream. Of the eight heavy metals, only chromium, selenium, and mercury exceeded the maximum allowable concentrations in the U.S. Environmental Protection Agency (EPA) Extraction Procedure [*11*]. These simple, untailored grouts showed a low-exchange capacity for these three elements, since the pickling liquor waste stream was highly saturated with soluble heavy metal chlorides whose relative concentrations were higher than the other two waste streams. Since higher than normal concentrations of the heavy metals were used in all of the simulated waste streams, many of the grout's exchange capacities may have been oversaturated. For this reason, real waste final concentrations could be expected to be lower than these tests indicate. This is particularly significant in light of the fact that the leach tests generally resulted in concentrations less than the maximum allowable concentrations in the EPA-Extraction Procedure (that is, 100 times EPA drinking water stan-

TABLE 7—*MCC-1 static 28-day leach concentrations, ppm.*

Element	Fly Ash	Limestone Scrubber	Pickling Liquor
Al	1.15 ± 0.15	1.18 ± 1.01	12.2 ± 3.1
As	0.0494 ± 0.0076	0.0433 ± 0.0724	0.516 ± 0.223
Ca	9.60 ± 5.82	498 ± 25	49.2 ± 19.3
Cd	nd[a]	nd	nd
Cr	29.0 ± 5.7	224 ± 184	118 ± 21
Cu	nd	nd	nd
Fe	nd	nd	nd
Hg	0.544 ± 0.161	3.81 ± 1.81	12.8 ± 1.8
Mg	6.36 ± 1.49	6.38 ± 1.26	7.77 ± 0.6
Mn	0.00529 ± 0.00375	0.0230 ± 0.0377	2.41 ± 3.23
Na	110 ± 5	234 ± 77	2612 ± 54
Pb	0.0258 ± 0.0077	0.282 ± 0.391	2.29 ± 0.37
Se	1.48 ± 0.33	11.7 ± 7.9	24.1 ± 2.1
Si	8.71 ± 0.92	8.61 ± 1.53	7.17 ± 1.57

[a]Not detectable.

dards). Since these leach tests determined saturation values, the resulting concentrations would be expected to be significantly higher than those obtained in the shorter (<24 h) EPA extraction procedure. Therefore, with actual waste and the proper cement-based, dry-solid blend, it is not unreasonable to expect that in the EP-extraction procedure the leachate in direct contact with the tailored grout could approach or meet drinking water standards.

Organic Waste—With the exception of dichlorofluorene, the leach data for the spiked oil specimens indicated that the organics in the leachate (obtained by liquid chromatography) were below detection limits. The combination of the general insolubility of most of these organics in the grout pore water (pH > 11) and the retentive ability of the grout is believed to be responsible for the low organic concentrations. Table 8 indicates the maximum concentration or detection limits for each of the six organics in the leachates. Al-

TABLE 8—*Maximum toxic organic concentration in leachate.*

Organic Compound	Concentration, ppb
Tetrachlorobiphenyl	<0.76
Hexachlorobiphenyl	<1.5
Octachlorobiphenyl	<1.5
Lindane	<0.76
Pentachlorophenol	<10 000
Dichlorofluorene	607 ± 215

though the data are insufficient for determining saturation concentrations, they do illustrate the technical feasibility of using cement-based grouts in the disposal of organics. Most organics are known to retard the set of cement pastes as defined by the ASTM Test for Time of Setting of Concrete Mixtures by Penetration Resistance (C 403). Consequently, it is a common misconception that organics and cement-based grouts are incompatible. However, the data clearly indicate that cement-based grouts can be compatible with wastes containing organics.

Conclusions

Results are presented which show that cement-based grout technology used routinely for the immobilization of radioactive wastes is applicable to industrial and hazardous wastes. Leach data illustrate that these grouts are capable of protecting the biosphere from the release of both heavy metals and toxic organics. This study used only simple grout formulations to fix these contaminants. With additional formulation studies, the ability of cement-based grouts to protect the biosphere from the release of these contaminants can be greatly increased. Therefore, immobilization of industrial wastes in cement-based grouts offers improved waste management by forming an effective barrier to the leaching of hazardous contaminates.

Acknowledgment

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Procedures for Characterizing Effects of Organics on Solidification/Stabilization of Hazardous Wastes

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ABSTRACT: The mechanisms whereby organic hazardous wastes interact with cement matrices is important for characterizing existing and future solidification/stabilization technologies and for evaluating these technologies using short-term testing techniques. In the complex chemistry of cement setting reactions, many phases are formed. Consequently it is necessary to use a variety of microscopic and microanalytical tools in studies of these systems. Methods employed in the present study are scanning electron microscopy, energy dispersive X-ray analysis, electron probe microanalysis, and X-ray powder diffraction. Examples of the application of these techniques to studies of cement containing *para*-bromophenol are presented. The organic appears to occupy several different environments, and an inhomogeneous distribution of the phenol among the phases of hydrated portland cement can be demonstrated.

KEY WORDS: solidification, stabilization, microscopy, scanning electron microscopy, phenols

The disposal of hazardous industrial wastes is a major concern of environmental engineers and scientists. Methods that produce stable, nontoxic products that do not expose the public to health risks must continue to be devel-

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oped and evaluated. A widely used method for treatment of contaminated liquids and sludges is solidification/stabilization. In this method, a hazardous sludge is mixed with a suitable second component or binding agent for the purpose of producing a stable, solidified end product. The final disposal of this end product is normally by placement in a secure landfill. Although solidification/stabilization followed by land disposal may not be as attractive a technique for managing organic hazardous wastes as incineration appears to be, it is felt that this approach will remain an important technology for years to come. This is true for a number of reasons:

- While the 1984 amendments to the Resource Conservation and Recovery Act address banning of land disposal of hazardous wastes, it is highly unlikely that all listed wastes will be banned in the future.
- Some hazardous wastes are not amenable to other types of treatment such as physical/chemical, biological, and incineration.
- In many cases, in-situ treatment or landfilling of wastes from abandoned sites may be the only feasible management technique.
- Residues from any hazardous waste treatment technique are defined as a hazardous waste and require land disposal.
- Alternate hazardous waste treatment and disposal techniques are often economically prohibitive.

Solidification/stabilization, usually employing cementitious fixing agents, is a commonly applied technology for the conversion of liquid hazardous wastes to solids before landfilling. Aqueous waste streams containing cations of toxic metals may be solidified relatively cheaply, and considerable data are available about the leachability of various metal ions from the solidified mass, with most of the data referring to proprietary stabilization processes. Mixed waste streams containing organics as well as inorganics are common, but little attention has been devoted to the effects of organics on commonly applied stabilization processes, despite the fact that organics are known to have profound effects on the setting of cements.

The purpose of this document is to describe the methods being utilized by the study group in their efforts to increase the scientific base of information about the nature of solidified/stabilized hazardous waste mixtures. Of primary importance is the understanding of bonding mechanisms and chemical waste entrapment along with a description of the kinetic processes that govern the leaching behavior of the end products.

Preparation of Solidified Materials

The organic chosen for the study was *p*-bromophenol (PBP). PBP was chosen because it is typical of an important class of water-soluble organic wastes and because bromine is easily detected by the energy dispersive X-ray ana-

lyzer in both scanning electron microscope (SEM) and electron probe microanalysis (EPMA).

PBP was solidified with a mixture of pure water and Type I portland cement. As a control, specimens were also mixed without the addition of the organic. Specimens were prepared by weighing the components and then placing them in 20×10^{-6} m^3 borosilicate glass, screw cap scintillator vials. The contents were then stirred with a glass rod and allowed to cure. The compositions included in the investigation were 0.2, 0.4, 1, 2, or 5 g of waste with 10 g of cement and 4 g of water. Curing times of at least 28 days (but sometimes up to 3 months) were allowed. The features to be described in the present report did not appear to change significantly as a function of curing time after 28 days.

Specimen Preparation for Microscopic Examination

Polarized Light Microscopy

The solidified waste samples were first polished to a smooth surface using 400 and 600 mesh abrasive papers. They were then glued to glass microscope slides, using Hillquist epoxy, and cured for 24 h. The bulk of the mounted specimen was then removed with a diamond saw. The remaining material was gradually ground away using 400, 600, and 1000 mesh abrasive papers, successfully. Final polishing was performed with 6-μm diamond paste, and 0.3 and 0.5 alumina powders on a polishing wheel. In all steps, isopropyl alcohol, instead of water, was used for cooling and lubricating. The final thin sections were approximately 30 to 40 μm thick. They were carbon coated for EPMA analysis.

Scanning Electron Microscopy

For analysis by SEM and energy dispersive X-ray (EDX) techniques (particularly quantitative analyses), a flat surface yields the most reliable results [*1*]. Preparation of specimens, therefore, began with polishing. At first, polishing consisted of taking a specimen mounted in a 1 in. (25.4 mm) by 1.3×10^{-2} m deep cylinder of plastic Kold Mount. The specimen was ground with a coarse grit paper, then finer grits, and then finally alumina particles on a wheel. After polishing, a 20-nm gold-palladium coating was applied to the specimen to prevent charging effects in the SEM.

Before polishing, the specimens were impregnated with a hard polymer to insure rigidity. The impregnation process consisted of the following steps. A small specimen (± 5 mm long and ± 2 mm thick) was taken from the center of the sample cylinder, was degassed in a vacuum chamber for about 1 h, then immersed in the polymer and placed into a vacuum oven (at ambient temperature) for 24 h. The specimen was then heated, under vacuum, to 60 ± 5°C

for another 24 h, then mounted, polished, and coated as previously described.

In some instances SEM of fractured, rather than polished, surfaces reveals additional information. To prepare these specimens, set cement samples were immersed in liquid nitrogen and allowed to chill for approximately 1 min. Tongs were then immersed, and the specimen was removed and immediately fractured. The resulting surfaces revealed little distortion and are believed to be representative of the actual structure [*2*].

Results

Light Microscopy and Electron Probe Microanalysis.

In Fig. 1, a light microscope image of a one month old specimen containing *p*-bromophenol is shown. Figure 1*a* reveals a bimodal grain size distribution with the coarser grains being elongated to an average length of 0.5 μm. Th·

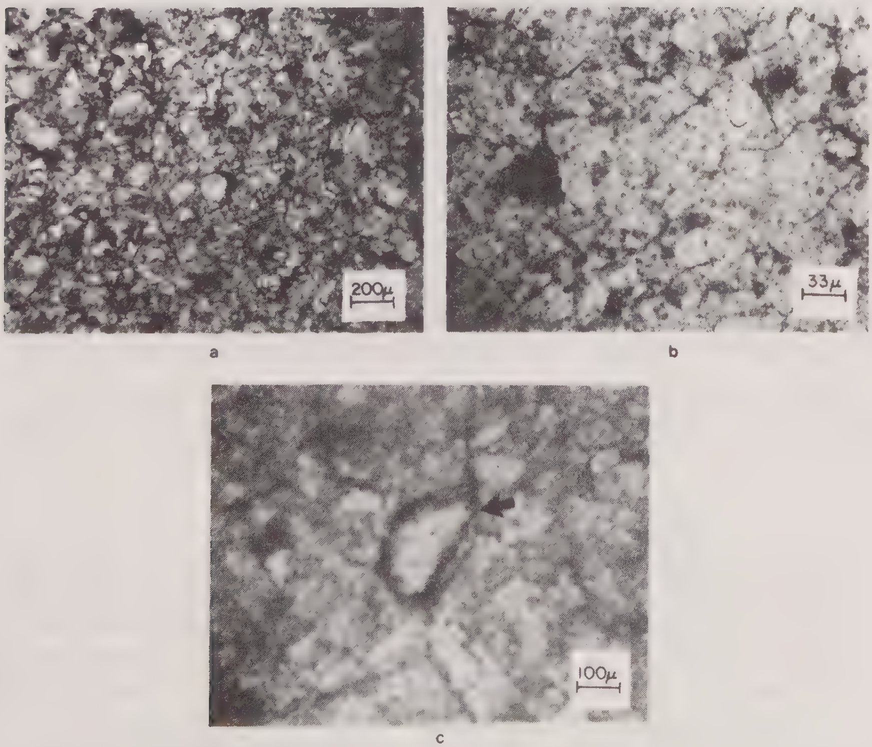

FIG. 1—*A cement/waste system containing 10% PBP:* (a) *a transmitted light micrograph showing a bimodal grain size distribution;* (b) *a grain with an enriched outer rim of organic waste (shown by the arrow); and* (c) *coarse, waste-rich grains within the cement.*

grains usually had a roughly spherical core that was surrounded by a clear, thick angular rim. EPMA showed the grains to be calcium silicates. With crossed polarizers, in the light microscope, weak first-order yellow interference colors were observed. In ordinary light some of these grains showed a greenish-yellow color. These same regions were shown by EPMA to contain bromine and were therefore rich in PBP. Some grains, for example, the one shown by the arrow in Fig. 1*b*, were clear in the center but had a bromine rich outer rim.

The bromine from the organic compound was present throughout the thin section but varied considerably in concentration. In some cases, it formed a phase of its own and in others appeared to be dilutely dissolved in the calcium-silicate-hydrate (CSH) gel phase. Coarse, greenish-yellow grains like those in Fig. 1*c* were found to be very rich in bromine and calcium. Table 1 shows compositional analyses of a control cement (containing no waste) and an analysis of bromine (organic) rich phases. Oxygen was determined by difference since it was not detectable by the spectrometers.

A fine grained matrix phase was observed although it could not be easily characterized using either optical microscopy or EPMA. Even at ×600 no distinct grain boundaries were visible. However, with crossed polarizers, very small domains of birefringence could be seen. This indicated the presence of distinct grains. No photomicrographs could be taken with crossed polarizers because of very low light levels.

Scanning Electron Microscopy

Figure 2 shows scanning electron micrographs of polished surfaces of a control cement. The general appearance of Fig. 2*a* correlates well with the optical micrograph of Fig. 1*b* where 1- to 10-μm grains are embedded in a fine-grained matrix phase. EDX analysis in the SEM corroborated the EPMA

TABLE 1—*EPMA of cement containing PBP.*

	Concentration, weight %	
Element	Control	Waste[a]
Si	9.0 ± 0.15	3.2 ± 1.3
Ca	37.9 ± 0.71	43.0 ± 3.14
Fe	1.8 ± 0.2	5.5 ± 1.3
S	0.4 ± 0.0	0.1 ± 0.2
K	0.1 ± 0.0	0.4 ± 0.2
Mg	1.8 ± 0.4	1.1 ± 0.2
Al	2.5 ± 0.3	0.4 ± 0.0
Br	0.0	33.9 ± 1.5
O	46.4 ± 1.2	12.2 ± 6.1

[a]The area being analyzed contains a bromine-rich grain referred to in the text.

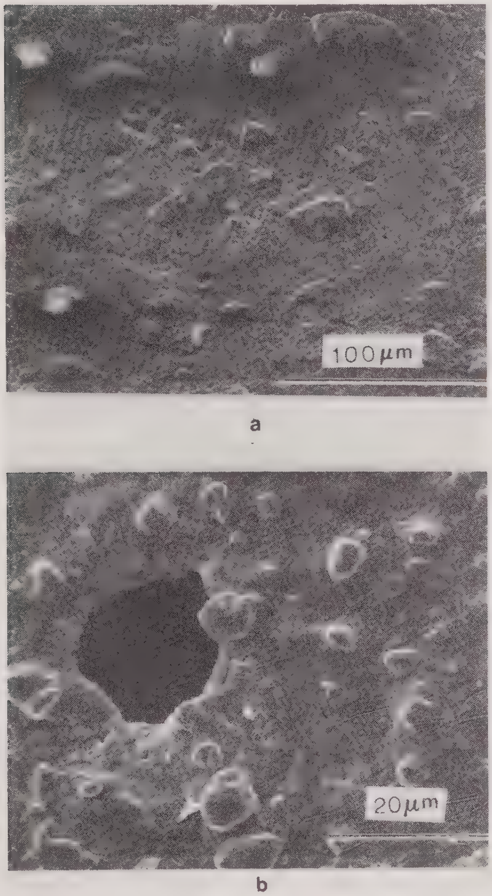

FIG. 2—*Scanning electron micrographs of a control cement:* (a) *calcium-silicates embedded in a matrix of calcium-silicate-hydrate gel phase, and* (b) *a pore caused by air entrapment during mixing.*

result that the large grains were calcium silicates. Figure 2*b* shows an approximately 20-μm-diameter pore similar to those shown by light microscopy. There is also a very fine scale porosity (1 to 10 μm) revealed in Fig. 1*b*, however, it was found that at either lower imaging voltage (in the secondary electron imaging mode) or using the backscattered electron imaging mode more fine scale porosity was observed. This is illustrated in Figs. 3*a* and *b*.

Careful examination of fracture surfaces also suggested a high degree of what appeared to be porosity. It is initially difficult to confirm, however, whether the features observed in fracture specimens are true pores or if they are dimpled fracture surfaces. Initially in order to resolve the issue we in-

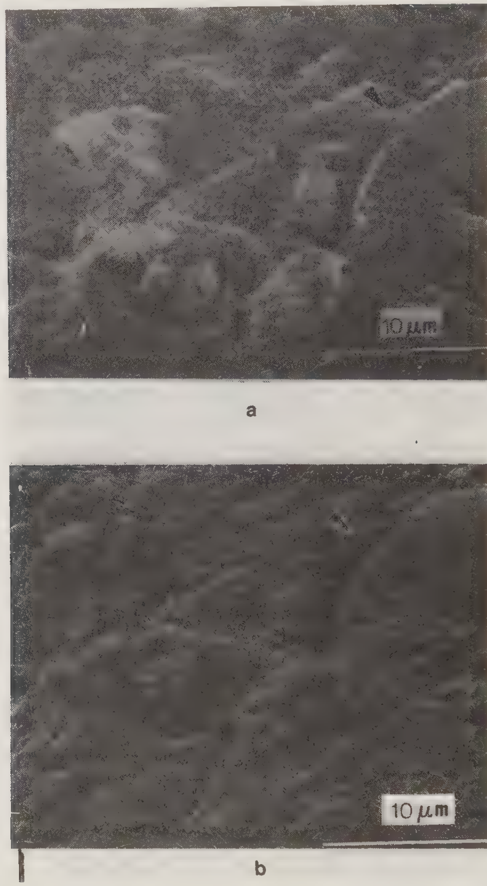

FIG. 3—(a) *Secondary electron image (15 KeV) and a* (b) *backscattered electron image (5 KeV) of a control cement aged one month. The backscattered electron image reveals a fine scale porosity. Arrows indicate a common feature for reference.*

tended to do stereo-pair SEM on both halves of the fractured solid. However, it was noted that at higher magnifications many of the features contained acicular crystallites (presumably ettringite) growing into the apparent void space. This confirmed the identification of the features as pores rather than fracture dimples (which could not contain such crystallites). This is illustrated in Fig. 4.

Figure 5 is an SEM micrograph of a 1-month old cement containing 10% PBP. The microstructure is similar to that shown in the previous micrographs of control cements. Many 5- to 10-μm calcium-silicate particles are embedded in the matrix phase of calcium-silicate-hydrate gel. Figure 5*b* is the bromine X-ray dot map of the same region. The presence of bromine indicates the

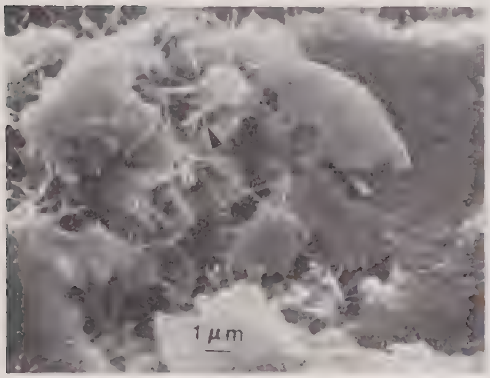

FIG. 4—*Fine crystallites of ettringite in a cement containing 10% PBP.*

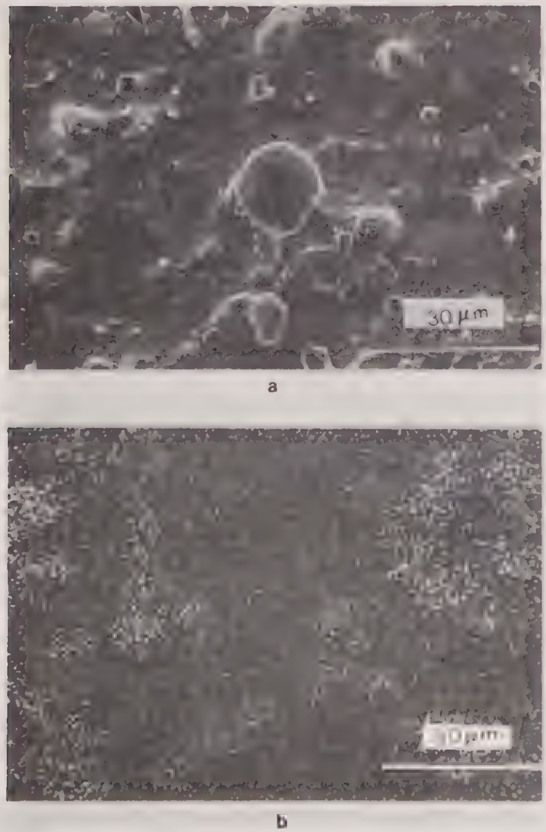

FIG. 5—*A 10% PBP sample aged one month:* (a) *a secondary electron image (at 15 KeV) and* (b) *is the bromine X-ray dot map.*

microscopic distribution of organic in the gel phase. Two features are to be noted. First, there are large organic concentration variations within the gel phase. Second, there is no evidence for organic existing within the highly crystalline calcium-silicate inclusions. Control experiments have revealed that the low-density distribution of dots in the map is instrument noise and can be ignored.

Discussion

Cement/waste systems form complicated polyphase mineral structures that are difficult to characterize using a single microscopic or microanalytical method. Combined use of optical microscopy, EPMA, SEM, and EDX analysis can, however, define the microstructure.

It is observed that the cements, both control and waste containing, have three levels of porosity. Pores greater than 10 μm in diameter exist because of air entrapment. They are usually spherical in shape. Pores also exist on a 1 to 10 μm level. These pores are usually irregularly shaped and frequently contain clusters of acicular crystallites. These crystallites have popularly been identified as ettringite [*2*]. The identification is based on X-ray diffraction analysis which does confirm the presence of ettringite in the bulk. However, identification, using EDX, of the small acicular crystallites as ettringite is highly suspect. This is due to unavoidable beam penetration of the analyzed region, that is, the analysis is coming from a volume of material greater than the volume of the crystallites being studied.

Finally, there is a distribution of pores which is less than 1 μm in diameter. These pores have been previously overlooked because of high primary electron beam voltages.

The interiors of pores of the two larger sizes were carefully analyzed using EDX, and none were found to contain unusually high concentrations of organic. The smallest pores were too small to be probed with EDX. It is concluded from these results that the wastes are not primarily stabilized by physical entrapment in pores of micron size. If the small pores do contain entrapped wastes it is unlikely that the waste is available for leaching in the unfractured material because there is no evidence of small pore interconnectivity.

Using a combination of light microscopy, EPMA, SEM, and EDX, it is observed that organic material is bound in the matrix in two distinct forms. A concentrated very localized phase containing approximately 34% waste was observed. This form was distributed as both equiaxed and irregularly shaped grains. In addition, the observation in Fig. 1*b* of grains with a bromine-rich outer rim suggests the possibility that the concentrated waste phase consists of the calcium salt of PBP crystallizing on the surface of a normal cement

component (either unhydrated cement grain or calcium hydroxide) rather than simply poorly dispersed and largely unreacted PBP.

The second form of stabilized waste is a heterogeneous distribution, in the CSH gel, of regions containing approximately 3 weight percent organic. The gel phase is a poorly defined phase in which is embedded very small crystallites of various calcium aluminosilicates. Consequently, it is very likely that the waste is segregating to specific phases within the gel itself.

A detailed crystallographic identification of neither of these waste phases has been accomplished to date.

Summary

It is shown that careful use of several combined microscopies and microanalytical techniques can provide a method for identifying mechanisms of waste stabilization. Using model waste/binder systems of *p*-bromophenol and Type I portland cement, it is found that two waste phases are produced. One is quite concentrated and occurs as large grains. The second is a submicroscopic, heterogeneous distribution of organic within the gel phase. Preliminary evidence is that the former phase can be called a waste phase and is unlikely to be merely a modification of a normally existing cement mineral component. The second phase, however, may be a solid solution of waste molecules in the CSH gel phase, which is the predominant mineral component of hydrated portland cement pastes.

These results are important to the understanding of how current solidification technology might provide a means for the permanent disposal of certain hazardous wastes.

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Process Technology for the Biological Treatment of Toxic Organic Wastes

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ABSTRACT: The problem of toxic waste disposal is one which has global implications regarding the preservation of the integrity of the environment. Concomitantly, it has become increasingly obvious that, because of the economics of water pollution control, biological treatment processes will be expected to incur an ever-increasing share of the task of purifying waste streams. With increasing industrialization, waste streams will more frequently contain organic compounds that are classified as toxic or inhibitory. The purpose of this report is to present and collate the results of several year's work in our laboratories that concerned the aerobic biological treatment of toxic organic wastes. Based on this work, it is feasible to suggest a number of engineering strategies applicable to the biological treatment of inhibitory organics. The thrust of this paper is to present this information in such a way that it can be readily utilized by pollution control professionals for designing and operating aerobic biological systems for treating biodegradable toxic organics.

In the first portion of the paper, the kinetics of microbial growth on toxic, or inhibitory, wastes and on nontoxic, or "conventional," wastes are compared and contrasted by illustrating both the differences and similarities with the biodegradation kinetics of these different types of wastes. In order to have the ability to recommend relevant treatment models for the purpose of designing and operating effective treatment facilities, it is essential to characterize the nature, that is, inhibitory or noninhibitory, of microbial growth kinetics on a particular waste. Consequently, this portion of the paper delineates the criteria that are utilized to categorize a waste as toxic or nontoxic.

A key requirement for the design and operation of biological treatment facilities is to have a relatively accurate assessment of both the range and variability of the biokinetic constants that characterize the biomass that is responsible for purification of a particular waste. These constants can be classified as the biokinetic growth constants and the maintenance constants. The latter group is responsible for quantifying sludge production in a biological treatment system while the former group quantifies the relationship between biomass growth rate and exogenous substrate (waste) concentration. Methods for evaluating the maintenance constants are relatively straightforward and are the same for both inhibitory and noninhibitory wastes. The situation is different, however, for the biokinetic

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growth constants. For noninhibitory wastes, only two biokinetic constants, μ_{max} and K_s, are utilized in the growth rate function (Monod equation), whereas for inhibitory wastes three biokinetic growth constants, μ_{max}, K_s, and K_i, are contained in the inhibition growth function (Haldane equation). This makes the kinetic analysis and the task of biokinetic constant evaluation for inhibitory compounds more difficult. In this section of the paper, a number of methodologies are presented that can be used for collecting growth data and for evaluating the biokinetic constants for acclimated population growing on inhibitory compounds.

The final portion of the paper concerns the development and application of design and operating equations that can be used for activated sludge processes treating toxic wastes. These are developed by inserting an inhibition growth function into the mass balance equations for an activated sludge reactor. The effect of the growth kinetics of toxic organics on activated sludge design and operation policies are illustrated via the utilization of dilute-out curves. Additionally, the genesis and application of critical point curves which quantify the operational location of the critical, or peak, growth rate μ^*, which characterizes activated sludge reactors treating inhibitory wastes, are shown; the use of these curves can maximize treatment efficiency while preventing sudden effluent deterioration and washout in activated sludge systems treating toxic or inhibitory wastes.

KEY WORDS: wastes, water pollution, disposal, biological treatment, toxic organic wastes, inhibitory substrates, predictive model, activated sludge

Nomenclature

- D Dilution rate; ratio of flow F to volume of liquor V in aeration tank, time^{-1}
- F Rate of flow in incoming substrate or waste water, volume $\times$ time^{-1}
- F_R Recycle sludge flow rate, volume $\times$ time^{-1}
- k_d Specific decay rate, time^{-1}
- K_i The inhibitor constant, used in the Haldane and other model equations for inhibitory substrates to account for the effect of concentration of the inhibitory substrate on the specific growth rate, mg $\cdot$ L^{-1}
- K_s The saturation constant, the shape factor in the rectangular hyperbola form of the Monod relationship; it is defined as the concentration of the limiting substrate at which $\mu = 0.5\ \mu_{max}$, mg $\cdot$ L^{-1}
- S Soluble substrate concentration, mg $\cdot$ L^{-1}
- S_e Soluble substrate concentration in the clarifier effluent; it is equal to the soluble substrate concentration in the reactor for a completely mixed reactor, mg $\cdot$ L^{-1}
- S_i Concentration of substrate in inflowing feed to a biological reactor, mg $\cdot$ L^{-1}
- S_R Soluble substrate in the biological solids recycled to the reactor, mg $\cdot$ L^{-1}
- $\bar{t}$ Nominal aeration tank detention time F/V, time
- V Aeration tank volume, L
- X Biological solids concentration in reactor, mg $\cdot$ L^{-1}
- X_R Biological solids concentration in recycle flow to reactor, mg $\cdot$ L^{-1}
- X_w Excess biological solids (sludge wasted), mg $\times$ time^{-1}
- Y_t True cell yield, mg $\cdot$ mg^{-1}

α	Recycle flow ratio, F_R/F
Θ_c	Mean cell residence time; it is the reciprocal of the net growth rate μ_n time
μ	Specific growth rate, time^{-1}
μ^*	Critical growth rate, time^{-1}
μ_{max}	The maximum specific growth rate of which a biomass is capable under specified conditions of temperature and pH in the absence of any restriction on growth rate by limiting nutrient concentration, for example, oxygen, nitrogen, or carbon source, time^{-1}
μ_n	The net specific growth rate, time^{-1}
μ_n^*	Critical net growth rate, time^{-1}

Introduction

The use of biological processes for the treatment of toxic or inhibitory wastes can offer a number of advantages over alternative treatment technologies such as physical-chemical treatment and incineration. Biological systems are not only capable of waste detoxification but are also potentially capable of complete oxidation of toxic organic matter. For some aqueous wastes, a biological treatment process, such as an activated sludge system, may prove to be the only cost-effective treatment technology. In order to realize successful process performance, it is mandatory to understand the kinetics of biodegradation of toxic substrates and their application to biological waste treatment processes.

The purpose of this paper is to review and collate the results of several years work by the authors on the biological treatment of an inhibitory or toxic carbon source, phenol. It should be noted that some organic pollutants that are duly classified as toxic in a regulatory sense can be metabolized by microorganisms but can inhibit the growth rate of acclimated populations at relatively high substrate concentrations; consequently, insofar as biological treatment processes are concerned some "toxic" organics may be designated as inhibitory organics. In this paper the terms are used interchangeably. In this report, the differences and similarities in the biodegradation kinetics of conventional and toxic pollutants will be discussed, along with methodologies that can be utilized for quantifying the inhibitory kinetics that are exerted by toxic organics. Also, the genesis and application of predictive equations that can be utilized for the design and operation of activated sludge systems treating inhibitory organics are given. Finally, the concept of critical point analysis and its relevance to biological treatment of toxic wastes is presented; the use of this concept in design and operation can maximize process performance efficiency while concomitantly avoiding sudden effluent deterioration and reactor failure, which can occur when the critical growth rate μ^* is exceeded in a biological reactor.

Engineering Significance of the Inhibitor Growth Function

For some time, there was disagreement among workers with regard to the necessity of utilizing an inhibition function for relating specific growth rate μ to substrate concentration S for toxic substrates. One school of thought advocated the use of the Monod function for this purpose [*1–3*], while others [*4–6*] suggested the use of inhibition function such as the Haldane equation. After extensive investigation, we concluded that the Haldane equation was the best inhibition function for representing the growth kinetics of acclimated heterogeneous populations on phenol [*7*].

To some extent, the two opposing modelling strategies can be reconciled by noting that, in low substrate concentration ranges, both models, the Monod (Eq 1) and the Haldane (Eq 2) exhibit similar predictive behavior; this is illustrated by the curves depicted in Fig. 1. Additionally, for high values of the inhibition constant K_i, the Haldane equation reduces to the Monod equation. However, if the biodegradation of toxics is examined with biological systems which are characterized by low growth rates, it is easy to conclude that either model would suffice. Also, because of the inhibition kinetics exhibited by toxic organic substrates, it is impossible to observe growth rates over a relatively large substrate concentration range in once-through chemostats; this point was made by Jones et al. [*4*] and Yang and Humphrey [*6*]. Thus, by the nature of a certain experimental approach, that is, the exclusive use of

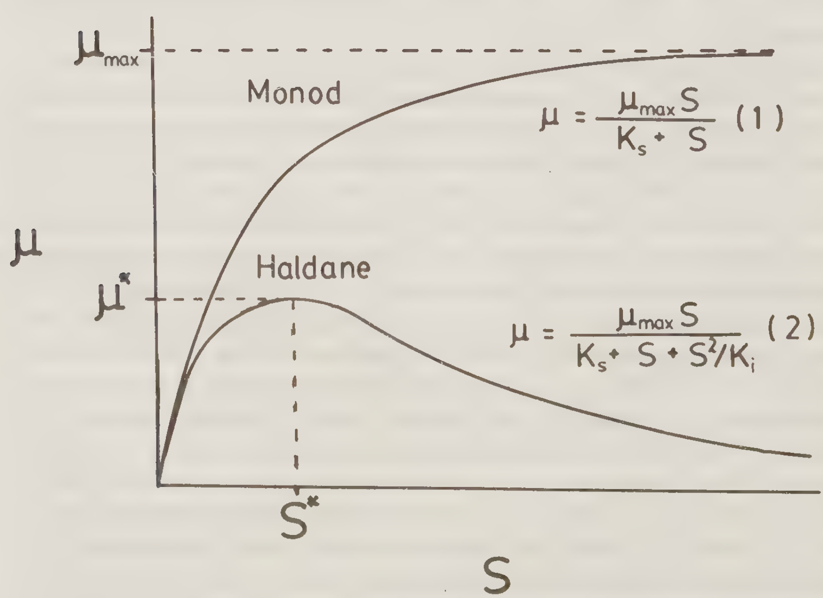

FIG. 1—*Comparison of Monod (nontoxic) and Haldane (toxic) growth rate functions.*

continuous flow reactors for collecting growth data for the study of toxic organics, some investigators may have inadvertently utilized a system that was incapable of producing growth data that could be employed for selecting a suitable growth rate function.

The differences in behavior of the two growth models for continuous flow systems are illustrated by comparing the dilute-out curves of toxic and nontoxic substrates in a chemostat; the predictive equations and the details of their derivation can be found elsewhere [*8*]. The curves presented in Fig. 2 compare the reactor substrate concentrations predicted by the Monod and Haldane-based equations for a chemostat; the values of the biokinetics constants used for the calculations are given in Table 1. For the toxic or inhibitory substrate (depicted by the Haldane equation), it is evident that treatment efficiency is maintained until an operating condition is reached, which results in sudden effluent deterioration and reactor failure ($S = S_i$); conversely, for the nontoxic (Monod) system, effluent deterioration is gradual until the system washes out. It should be pointed out that the inhibitory system washed out almost immediately after the chemostat attained the critical growth rate, μ^* (Fig. 1), which is specified by the inhibition function, that is, washout occurred when the dilution rate, $D = \mu^* - k_d$, where k_d is the specific decay

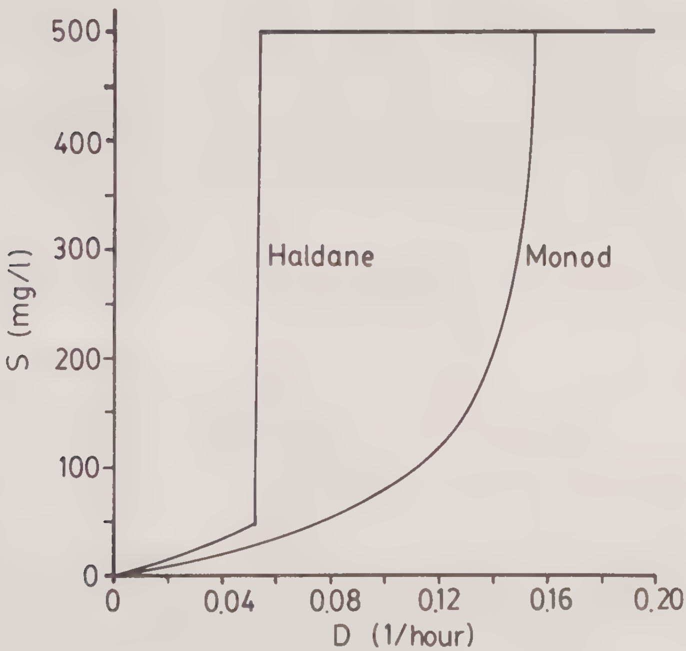

FIG. 2—*Comparison of predicted dilute-out behavior of Monod and Haldane growth rate functions in a chemostat. Biokinetic constants are given in Table 1.*

TABLE 1—*Values of biokinetic constants.*

Constant	Value
μ_{max}, h^{-1}	0.1940
K_s, mg/L	48
K_i, mg/L	62
Y_t, mg/mg	1.02
k_d, h^{-1}	0.0195

rate. It needs to be stressed that the critical growth rate μ^* is much less than the value of the maximum specific growth rate μ_{max}; consequently, it should be readily apparent that attempts to describe kinetics of biodegradation for toxic organic matter with the Monod equation would greatly overestimate the effective operating range for the reactor. The reason a continuous flow system treating inhibitory organics is prone to effluent deterioration once the reactor net growth rate approaches $\mu^* - k_d$ or μ_n^*, is that "past" this operating point, small increases in reactor substrate concentration only serve to depress growth rate, which causes further increases in substrate concentration; in the case of chemostats, violation of μ^* results in complete reactor failure. In other continuous flow reactor configurations, for example, cell recycle systems, violation of μ^* causes exceptionally high effluent substrate concentrations, which for practical purposes, can be considered a reactor failure. Thus, assessment of this parameter and the delineation of its relationship to the appropriate engineering control parameters is a key consideration with regard to the design and operation of effective facilities for toxic waste treatment.

An equation for quantifying μ^* in terms of the biokinetic growth constants, μ_{max}, K_s (the saturation constant), and K_i (the inhibition constant), is obtained by noting that the derivative at the peak of the growth curve (Haldane equation, Eq 2) equals 0. Expressions for μ^* and S^*, the substrate concentration associated with μ^*, are given in Eqs 3 and 4

$$\mu^* = \frac{\mu_{max}}{1 + 2\sqrt{(K_s/K_i)}} \tag{3}$$

$$S^* = \sqrt{K_s K_i} \tag{4}$$

In order to obtain a reasonable estimate of μ^*, it is important to obtain a satisfactory appraisal of both the value and range of variation of the biokinetic growth constants. Methodologies for assessing these constants have been developed in our studies.

Evaluation of Biokinetic Constants

The biokinetic constants that must be evaluated include the cell yield and specific decay rate, which are utilized for estimating waste sludge quantities, and the biokinetic growth constants, which are employed for relating μ to S. For toxic wastes, the values of the true cell yield Y_t and the specific decay rate k_d can be determined using methods that are described elsewhere [9,10]. However, the Haldane equation utilizes three constants, μ_{max}, K_s, and K_i, and additional consideration is required when collecting and analyzing growth data for the purpose of evaluating these biokinetic constants.

The initial step in evaluation of biokinetic growth constants is to collect a set of growth data (μ versus S) that is suitable for analysis. Batch methods are preferred, since they allow the analyst to assess both the range and variability of the biokinetic growth constants. Also, insofar as inhibitory substrates are concerned, chemostat growth data are inadequate since this system cannot "complete" the growth curve because washout will occur once μ^* is attained. The chemostat system is incapable of generating growth data applicable to the downward side of the inhibition function, that is, data to the right of μ^* on a plot of μ versus S. Batch growth data can be generated using the batch growth study, or shake flask, technique [7], or by analysis of substrate utilization data. The former method can be applied to inhibitory wastes whose characteristics are such that they permit sufficient cell growth to allow the determination of a specific growth rate via the measurement of the time course of increase in biomass concentration; this method has been successfully applied for determining the biokinetic growth constants for phenol [7]. In the alternate method, batch substrate utilization data are used to present graphically the specific substrate utilization rate at given substrate and biomass concentrations; these specific substrate utilization rates are converted into specific growth rates by knowing or estimating the cell yield and utilizing Eq 5

$$\mu = -\frac{Y_t}{X}\frac{dS}{dt} \tag{5}$$

This method is useful for wastes that do not permit sufficient biomass growth to employ the shake flask technique.

Once the μ versus S data are collected, they must be fitted to the Haldane equation in order to evaluate μ_{max}, K_s, and K_i. Because this equation contains three constants, the best approach for fitting the data appears to be the application of a bounded nonlinear least squares regression technique [7]. In applying this technique, the nonlinear least squares algorithm searches for a minimum of least squares only within a bounded domain of allowable values for the constants. A bounding program can be written that rejects physically meaningless results, for example, negative values for the biokinetic con-

stants. An example of this procedure and the computer program that was used for evaluating the biokinetic growth constants for phenol are given elsewhere [7]. By applying this technique, a unique set of values can be obtained for the three biokinetic constants within the chosen allowable domain.

Activated Sludge Treatment of Toxic Wastes

Equations that can be utilized as guides for the design and operation of activated sludge processes for treatment of toxic wastes are derived by first writing steady state mass balances for biomass and substrate around the reactor, which is depicted in Fig. 3, and inserting an appropriate growth rate equation for relating μ to S. It should be noted that the flow diagram depicted in Fig. 3 advocates the control of recycle sludge concentration X_R, via the utilization of an in-stream dosing tank; this control technique has been shown to be extremely effective in maintaining consistent substrate utilization rates and process stability [*10,11*]. Thus, in systems exhibiting inhibition kinetics, control of X_R is strongly recommended since it can help prevent process failures for activated sludge systems treating toxic wastes.

Predictive equations for the reactor biomass concentration X and the substrate concentration S are obtained by solution of the mass balance equations; details regarding the development of the predictive equations are given elsewhere [*10*]; a listing of design and operating equations for activated sludge processes for both toxic and nontoxic wastes is given in Table 2.

It is interesting to compare the dilute-out behavior of the toxic (Haldane) and nontoxic (Monod) activated sludge process equations. In Fig. 2, the dilute-out behavior of the two growth models was compared in a chemostat, where it was shown that the inhibition model predicted a much narrower op-

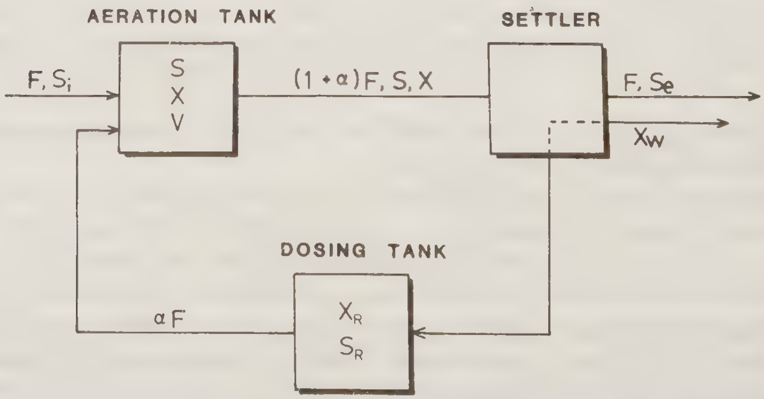

FIG. 3—*Flow diagram of activated sludge process that uses control of recycle sludge concentration.*

TABLE 2—*Steady state predictive equations for constant* X_R *continuous-flow systems.*

Inhibitory Substrate (Haldane)		Noninhibitory Substrate (Monod)	
$S\colon aS^3 + bS^2 + cS + d = 0$	(6)	$S = \dfrac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$	(7)
$a = \dfrac{(1+\alpha)[(1+\alpha)D + k_d]}{K_i}$		$a = ([(1+\alpha)D + k_d] - \mu_{max})(1+\alpha)$	
$b = [(1+\alpha)D + k_d]\left(1 + \alpha - \dfrac{(S_i + \alpha S_R)}{K_i}\right) - (1+\alpha)\mu_{max}$		$b = \mu_{max}\left(S_i + \alpha S_R + \dfrac{\alpha X_R}{Y_t}\right) + [(1+\alpha)D + k_d][(1+\alpha)K_s - (S_i + \alpha S_R)]$	
$c = \mu_{max}\left((S_i + \alpha S_R) + \dfrac{\alpha X_R}{Y_t}\right) + [(1+\alpha)D + k_d][(1+\alpha)K_s - (S_i + \alpha S_R)]$		$c = -(S_i + \alpha S_R)[(1+\alpha)D + k_d]K_s$	
$d = -(S_i + \alpha S_R)[(1+\alpha)D + k_d]K_s$		$X = \dfrac{Y_t[S_i + \alpha S_R - (1+\alpha)S] + \alpha X_R}{1 + \alpha + k_d/D}$	(6a)
$X = \dfrac{Y_t[(S_i + \alpha S_R) - (1+\alpha)S] + \alpha X_R}{1 + \alpha + k_d/D}$	(6a)	$X_w = VX\mu_n$	(8)
$X = VX\mu_n$	(8)		

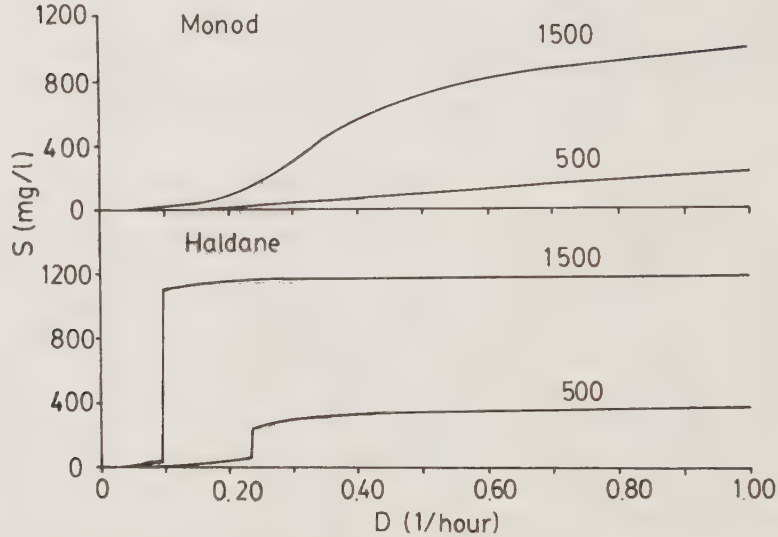

FIG. 4—*Comparison of dilute-out curves calculated from the Monod and Haldane equations for a constant* X_R *activated sludge process at* S_i *values of 500 and 1500 mg/L of phenol. Values of parameters are* X_R = *6000 mg/L and* $\alpha = 0.25$. *Biokinetic constants are given in Table 1.*

erating range than the Monod-based model. Figure 4 depicts the predicted dilute-out patterns for S, the effluent substrate concentration, for S_i values of 500 and 1500 mg/L for an activated sludge system. The values of the engineering control parameters, the sludge recycle flow ratio α and X_R are 0.25 and 6000 mg/L, respectively, for all plots; values for the biokinetic constants are given in Table 1.

The comparison shown in Fig. 4 illustrates a number of important points regarding toxic waste treatment. It is evident that the two growth rate expressions predict radically different behavior in the activated sludge reactor. The inhibition equations predict that adequate treatment efficiency is maintained until an operating point is reached where sudden effluent deterioration occurs; this effect is exacerbated with increasing waste strength S_i (Fig. 4). This behavior is not predicted with the Monod-based equations, which by contrast suggest a much less radical decay in effluent quality. It can also be shown that, as was the case for the chemostat equations, the rapid degeneration in effluent quality for the activated sludge system, which was predicted by the Haldane-based equations, can be correlated with the point at which the reactor net growth rate reaches $\mu^* - k_d$. Additionally, it should be stressed that bench-scale pilot plants in our laboratory [*8,11*] that were acclimated to the toxic compound phenol and operated in the proximity of their critical net growth rates underwent rapid effluent deterioration which, for all practical purposes, resulted in reactor failure.

In all cases, the critical operating point was predicted rather well by utilizing the values of the biokinetic growth constants that were determined in separate batch growth studies [*8,11*]. Consequently, it is feasible to utilize the predictive model to formulate design and operating policies for toxic waste treatment, which can avoid operation near the critical growth rate and circumvent reactor failure. These strategies can be formulated with the aid of a critical point analysis [*12*].

Critical Point Analyses

A critical point analysis is simply a technique for quantifying the operational location of the critical net growth rate in an activated sludge reactor which is treating a toxic waste. This analysis quantitates that combination of the values of the biokinetic constants, the influent waste strength S_i, and the engineering control parameters α, X_R, and $\bar{t}$, the nominal hydraulic detention time, which results in the critical net growth rate in the aeration tank. The equations that predict the critical operating point are derived by using the biomass and substrate mass balance equation for the activated sludge reactor and substituting the analytical expressions for μ^* and S^* (Eqs 3 and 4, respectively) into these equations for μ and S, respectively; details regarding the genesis of the critical point equations are given elsewhere [*12*]. A critical point equation solved for the dilution rate D (reciprocal of the detention time) is given in Eq 9

$$D = \frac{1}{\bar{t}} = \left(\frac{1}{1+\alpha}\right)\left[\left(\frac{\mu_{\max}}{1 + 2\sqrt{\dfrac{K_s}{K_i}}}\right)\left(1 + \frac{\dfrac{\alpha X_R}{Y_t}}{S_i + \alpha S_R - (1+\alpha)\sqrt{K_s K_i}}\right) - k_d\right] \tag{9}$$

Equation 9 could also have been solved for either of the other engineering control parameters α or X_R. In this instance, the dilution rate (reciprocal of detention time) was selected because it is a relatively familiar control parameter; however, one could have easily derived critical point equations in terms of α or X_R, since the final form of Eq 9 is essentially left to the discretion of the individual analyst. Regardless of the form of the critical point equation, it can be used to construct critical point curves that can conveniently illustrate design and operational strategies, which can serve as guidelines for avoiding operation near μ^*.

A critical point curve is a graphical guide that quantifies the critical operating point, that is, the values of the engineering control parameters at which the reactor growth rate equals μ^*, the peak growth rate predicted by the inhibition function. For illustrative purposes, consider the graph depicted in Fig.

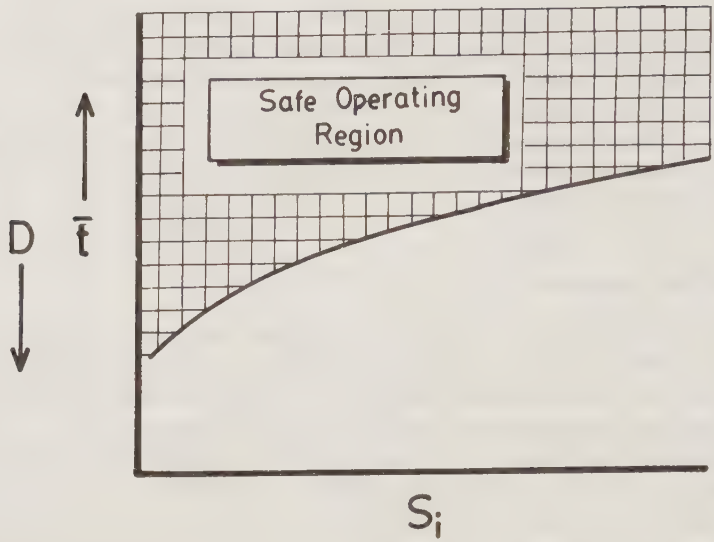

FIG. 5—*Critical point curve for activated sludge reactor treating an inhibitory waste. The curve is defined by substitution of appropriate biokinetic constants and selected values of* α *and* X_R *into Eq 9.*

5; the plot of the solid line that gives the values of $\bar{t}$ (for constant values of α and X_R) at which the reactor attains μ^* at different S_i values can be generated using Eq 9. The crosshatched area above the curve comprises a safe operating region where the reactor is not apt to experience sudden effluent deterioration and fail; conversely, operating conditions that are on or below the curve risk operational failure because of violation of the μ^* limit. Consequently, operation well above the curve is necessary in order to prevent reactor failure.

To demonstrate the use of critical point curves for design and operation of toxic waste treatment, consider the plots depicted in Fig. 6. These curves were constructed by using the values of biokinetic constants for phenol listed in Table 1 and Eq 9. The recycle substrate concentration S_R was assumed to be negligible, that is, $S_R = 0$. A recycle ratio of $\alpha = 0.25$ was employed for all curves and recycle sludge concentration values were varied from 6000 to 30 000 mg/L. Figure 6 depicts a number of operational options that can be implemented in order to avoid a reactor failure. Consider an activated sludge reactor operating at an X_R of 6000 mg/L, α of 0.25, S_i of 1000 mg/L, and detention time of 10 h ($D = 0.10$ h^{-1}). If the influent waste concentration S_i increased to 2000 mg/L, the system would be pushed beyond the critical operating point and would fail. However, a design decision to increase reactor detention time to 13 h would alleviate operation near the critical point. Similarly, if the plant were operational, it is feasible to increase X_R to 10 000

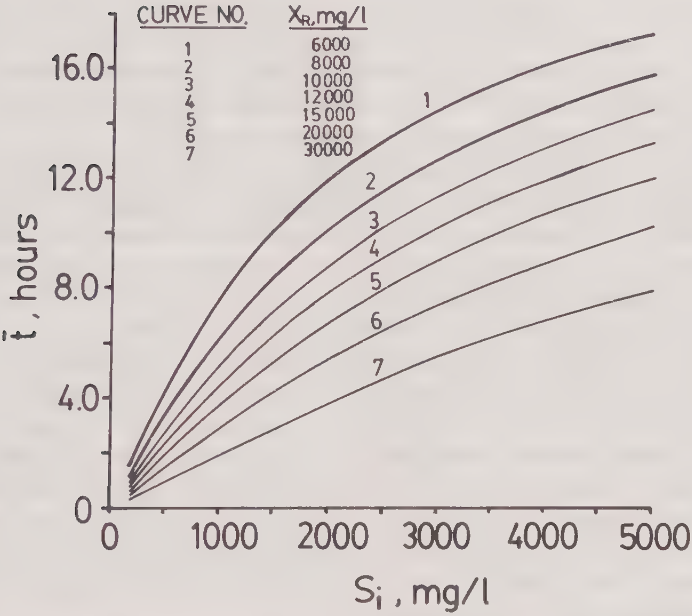

FIG. 6—*Critical point curves showing effects of* X_R *on location of critical operating point;* α = *0.25 for all curves.*

mg/L. The execution of either of these options will place the reactor in a safe operating region because it will be above the critical point curve. The recycle flow ratio α can also be utilized for averting critical operating conditions in the aeration tank; an illustration of the use of this control parameter for avoiding "blow-out" conditions is given elsewhere [*12*]. Thus, a change in either α, X_R, or $\bar{t}$ (that is, D) can be employed to prevent failure, which would otherwise be forthcoming because of a change in loading conditions, that is, a shock load.

Future Considerations

The design and operational model for biological treatment of toxic wastes has been shown to be quite effective for predicting bench-scale pilot plant performance for an activated sludge system treating a waste containing phenol [*8,10,11*]. There is great need, however, for additional research and developmental work regarding the biological treatment of other inhibitory organic compounds. First and foremost, consideration must be given to testing the model on a variety of different toxic components; this should be done using both single- and multicomponent inhibitory wastes. Given the component diversity of "real" waste treatment situations, it is important from a technologi-

cal standpoint to evaluate the applicability of the model for "real" inhibitory waste, for example, coke plant wastes as well as those in the leachate of land disposal sites for hazardous wastes. Work such as this would foster an improved understanding of biodegradation kinetics for toxic wastes while expanding the scope of toxic waste treatment technology.

Another research aspect regarding the multicomponent nature of actual wastes concerns the prediction of the kinetics that will govern a biological reactor that is treating a mixture of toxic and nontoxic, or "conventional," pollutants. Given the increasing opportunities for more centralized treatment via the consolidation of different waste streams, treatment facilities may more frequently encounter influents that consist of mixtures of toxic and nontoxic, that is, more easily biodegradable, components; such a situation already occurs in the case of priority pollutant disposition at Publicly Owned Treatment Works (POTWs) but usually with very low concentrations of toxic organics. There is significant need to determine the applicability of the inhibition activated sludge model presented herein for predicting reactor performance wherein the proportion of toxic component approaches or exceeds that for nontoxic components. Research should be conducted to determine any possible changes to the model that may be needed in order to preserve its predictive capabilities for such waste mixtures.

Summary and Conclusions

In this paper, technological and engineering strategies and recommendations were presented for the aerobic biological treatment of toxic organic wastes. These strategies rest on recognizing the fact [*7,8,10,11*] that acclimated heterogeneous populations exhibit radically different growth kinetics on toxic organics and on nontoxic wastes. Methods were presented that can be used for quantifying the inhibitory nature of toxic wastes and for determining the values of the pertinent biokinetic constants, μ_{max}, K_s, and K_i. The remaining portion of the presentation concerned the development and application of design and operating equations that can be utilized for activated sludge processes treating toxic wastes. These were developed by inserting the Haldane growth rate equation, which accounts for the substrate inhibition caused by toxic organics, into the mass balance equation for an activated sludge reactor. The behavior predicted by these equations and the application of the equations to activated sludge design and operating policies for toxic waste treatment were illustrated by dilute-out curves. Finally, the application of critical point curves, which quantify the operational location of the critical, or peak, growth rate μ^*, which is characteristic of toxic waste treatment in activated sludge reactors, was demonstrated. It was shown that the use of these curves can maximize treatment efficiency while preventing sudden effluent deterioration and reactor failure in activated sludge systems treating toxic or inhibitory wastes.

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ASTM Test Method Development

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Developing Guides for Sampling and Analysis of Ground Water

REFERENCE: Bone L. I., "**Developing Guides for Sampling and Analysis of Ground Water,**" *Hazardous and Industrial Solid Waste Testing and Disposal; Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 337–342.

ABSTRACT: ASTM Committee D-34 on Waste Disposal has two subcommittees that are concerned with ground-water sampling: D34-02-08 on Groundwater Analysis and D34-01-01 on Environmental Monitoring and Sampling. Subcommittee D34-02-08 has been reviewing the Environmental Protection Agency's (EPA) Proposed SW 846 Method 8600 for screening ground water for Appendix VIII compounds. Subcommittee D34-01-01 has prepared Guides for Sampling Ground Water Monitoring Wells and Pore Water Sampling in the Vadose Zone. The ground-water guide discusses flushing requirements, well sampling devices, and sample container and preservation requirements. The author presents some of the guide's discussion concerning the advantages and disadvantages of sampling procedures and devices and offers some recommendations based on his own experience. Flushing 5 to 10 well volumes or until some parameter, such as pH or conductivity is stabilized, is recommended. Bailers, bladder pumps, or gas driven piston pumps are recommended, and the importance of preplanning sampling operations is emphasized.

KEY WORDS: ground water, solid waste, hazardous waste, monitoring wells, water quality, volatile organics, bailer, sampling pumps, sample preservation

Since its inception in 1980, ASTM Committee D-34 on Hazardous Waste has recognized that there is a need for standardizing ground-water monitoring practices. One does not have to be very familiar with the subject of ground-water monitoring to realize that our early recognition of such a need is well founded. You can simply read your newspaper and realize that there are numerous reports, and often fines, for improper or insufficient ground-water monitoring of hazardous waste facilities. Further, most of us involved in the subject are familiar with equally numerous indications of ground-water contamination, which really are just faults in the monitoring plan, that is, con-

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taminated sampling equipment, improperly installed or developed wells, and so forth. Thus it is clear that at least guidance, if not standards, are badly needed.

When the subcommittees of D-34 first started meeting, we not only recognized the need for standards but also realized that we could not take on the entire problem at once, but rather should undertake well defined projects that we could complete. The first task we choose was to develop standard procedures for sampling ground-water monitoring wells. We limited the scope of our first undertaking to sampling procedures starting with a properly installed and developed well and ending with samples ready for shipment to the laboratory. After considerable effort we came to the realization that there is not one standard practice for sampling ground-water monitoring wells, but rather a whole series of possible practices with varying degrees of acceptability depending on the location and depth of the wells and possible contaminants of interest. Consequently, we have developed a document entitled, ASTM Guide for Sampling Ground Water Monitoring Wells (D 4448). This guide was recently balloted at the committee level and should be available for publication before too much longer. The contents of this guide will be the subject of the majority of this paper.

ASTM Subcommittee D34-02-08 has devoted all of its attention to a review of the U.S. Environmental Protection Agency's (EPA's) Proposed SW 846 Method 8600 for screening ground water for Appendix VIII constituents. We received an early copy of Method 8600, also called the Hierarchical Analytical Procedure, from David Freedman at the EPA and thus were able to start evaluating some of the methods in the laboratory. Our first goal was to see if we could obtain good blanks and determine the frequency of false positives using realistic but uncontaminated ground water. Work carried out by Dow Chemical and Standard Oil Company (Indiana) found that a number of the methods were either acceptable or at least showed promise, but also found that one of the major procedures that involves a cartridge extraction followed by ultra violet (UV) spectroscopic screening had some major difficulties. We have since joined forces with Battelle Columbus Laboratories who was the EPA contractor evaluating the procedure. Battelle will coordinate a more extensive round robin to determine the UV adsorbance levels in clean ground water using the reverse cartridge procedure. While I think it is probably not ASTM's role to work so directly on an EPA proposed method, such an effort is well warranted in this case since the adoption of some method that would reduce the analytical burden associated with Appendix VIII compound identification is of prime importance to the regulated community.

Sampling Ground Water Monitoring Wells

The Standard Guide for Sampling Ground Water Monitoring Wells is limited in its scope to obtaining valid, representative samples from properly in-

stalled and developed wells. It further recognizes that there cannot be one standard practice for well sampling and thus the document is to serve as a guide for writing a site specific sampling plan. The guide is divided into three major areas: well flushing (purging), sampling equipment, and sample containers and preservation.

The well flushing section recognizes that for a sample to be representative of water in the formation, all standing water in the well must be removed before sampling. In general two approaches to flushing are recommended. For low yield wells emptying the well may be required but in doing so oxygen contact with the ground water needs to be avoided if oxidizable species are being monitored. In higher yield wells, removing 5 to 10 well volumes via an inlet near the water surface is generally sufficient, but purging until an indicator parameter, such as pH or conductivity reaches a steady value, is a good practice if such an indicator can be identified. When sampling a high yield well it is always necessary to be sure that the sample is withdrawn from a point at or below where the flush water was removed. Since fresh, formation water enters through the screen below the flush point, water above that point may be stagnant. In any flushing approach, a withdrawal rate that minimizes draw-down while satisfying time constraints should be used. This is because excessive draw-down distorts the natural flow patterns around a well and can even cause contaminants that were not present originally to be drawn into the well.

There are numerous devices available for ground-water sampling. The device used for sampling may or may not be the same device used for purging the well but in all cases must be carefully chosen considering a number of factors such as the depth of the well and the possible contaminants of interest. These factors can have a bearing both on the materials of construction and the device itself insofar as it agitates the sample, exposes it to air, or enhances the loss of volatiles.

In general the materials used to construct the wells, the purging devices, and the sampling devices should be inert to the full sampling environment and the use of adhesives should always be avoided. Although polyvinyl chloride (PVC) is often sufficient, Teflon®, stainless steel, or glass are usually preferable although there have been reports of difficulties with these materials also. The guide discusses some of these problems.

There is a wide range of sampling devices available for obtaining groundwater samples. The guide discusses these devices in eight categories: downhole collection devices, suction lift pumps, electric submersible pumps, gas-lift pumps, gas displacement pumps, bladder pumps, gas driven piston pumps, and packer pump arrangements. The guide does not suggest a particular device but rather discusses the advantages and disadvantages of each device in a way which we hope allows the user to select the proper sampling equipment for his individual circumstances. However, in this author's opinion, there are probably two preferred sampling devices unless the possible

contaminants are relatively simple or the entire sampling sequence is almost trivial. These are either a down-hole collection device (a bailer) or a noncavitation type of pump such as a bladder or a gas driven piston pump.

Bailers can be constructed out of a variety of materials and be equipped with check or messenger valves. They can be used at any depth, are easy to construct out of the material most inert in the sampling environment, and are reasonably good at preserving volatiles. It is this author's observation that stainless steel or Teflon®, double check valve bailers, dedicated to a specific well, are suitable for most sampling operations. However, it is often too tedious to flush a well using a bailer and thus some type of pump must be used in conjunction with the bailer. Either suction lift pumps or electric submersible pumps (depending on the depth of the well) are frequently satisfactory for flushing before sampling with a bailer. Although these pumps are usually not satisfactory for sampling because of potential loss of volatiles or exposure of the sample to noninert materials of construction (particularly in the pump's interior), these considerations are normally not important if the pump is used for flushing only.

The other type of device that this author favors is either a bladder pump or a gas driven piston pump since they are good at retaining volatiles and do not allow gases to contact the sample. The guide discusses the construction and method of operation of these devices as well as the advantages and disadvantages. In general models are now available using inert materials of construction, and they are quite good at preserving volatiles and preventing contact with oxygen. They are certainly more efficient at well flushing than the bailer but are still quite slow if large flushing volumes are required. We have purchased dedicated bladder pumps for use at the Petro-Processors, Inc. Louisiana Superfund Site. In shallow wells (less than 30.5 m [100 ft]) we are using the bladder pump alone. However in deep wells, since the time required to remove sufficient flush volumes is excessive, we have installed a permanent electric submersible pump above the bladder pump in each well.

The final item which the Standard Guide for Sampling Groundwater Monitoring Wells discusses is sample containers and preservation. Table 1, which is reproduced from the document, gives container and preservation requirements for most of the sample/measurement combinations encountered in ground-water applications. Probably one of the most important suggestions in the guide is contained in the container and preservation section. This is an emphasis on the importance of pre-planning of sampling operations. Preplanning starts with a written plan, and includes preparation of sample containers, pre-labeling, assembly of equipment, preparation of chain-of-custody papers, as well as coordination with the laboratory who will analyze the samples.

The need for filtering samples was the subject of considerable discussion during the preparation of the ASTM guide. It recommends that for samples, such as metals, radioactivity, and total organic carbon, where the emphasis is

TABLE 1—*Typical container and preservation requirements for a ground water monitoring program.*

Sample and Measurement	Volume Required, mL	Container P Polyethylene G Glass	Preservative	Maximum Holding Time
Metals (filtered on-site) As/Ba/Cd/Cr/Fe Pb/Se/Ag/Mn/Na	1000 to 2000	P/G (special acid cleaning)	high purity nitric acid to pH <2	6 months
Mercury (filtered on-site)	200 to 300	P/G (special acid cleaning)	high purity nitric acid to pH <2 +0.05% $K_2Cr_2O_7$	28 days
Radioactivity (filtered on-site) alpha/beta/radium	4000	P/G (special acid cleaning)	high purity nitric acid to pH <2	6 months
Phenolics	500 to 1000	G	cool, 4°C pH 0.5 to 4.0 with H_3PO_4, HCl, H_2SO_4, or $NaHSO_4$	48 h
Miscellaneous	1000 to 2000	P	cool, 4°C	
Fluoride	300 to 500	P		28 days
Chloride	50 to 200	P/G		28 days
Sulfate	100 to 500	P/G		28 days
Nitrate	100 to 250	P/G		48 h
Coliform	100	P/G		6 h
Conductivity	100	P/G		on site/24 h
pH	100	P/G		on site/6 h
Turbidity	100	P/G		48 h
Total organic carbon (TOC) (filtered on-site)	25 to 100	P/G	cool, 4°C or cool, 4°C HCl or H_2SO_4 to pH <2	24 h 28 days
Pesticides, herbicides and total organic halogen (TOX)	1000 to 4000	G/Teflon® lined cap solvent rinsed	cool, 4°C	7 days/extraction +30 days/analysis
Extractable organics	1000 to 2000	G/Teflon® lined cap solvent rinsed	cool, 4°C	7 days/extraction +30 days/analysis
Organic purgables acrolein/acrylo	25 to 120 ml	G/vial Teflon®-lined septum	cook, 4°C	14 days 3 days

on the concentration of the dissolved component, the samples should be filtered in the field or possibly at an on-site laboratory. The type or size of filter is not well understood, but it must not contribute species that interfere with the analysis, and the same filtering procedures should be used when successive analyses are to be compared.

Conclusion

Sampling ground-water monitoring wells is an exercise, which if done improperly can lead to considerable difficulty including large unnecessary expenditure of funds, bad publicity, and fines. Monitoring should always be carefully planned including a written monitoring and analysis plan that has been subjected to extensive review. It is equally important that additional planning and coordination among the various participants take place before each sampling period. The ASTM Guide to Sampling Groundwater Monitoring Wells has been written to aid the planning process.

Monitoring wells must be flushed before sampling such that the groundwater is sampled, not the stagnant water in the well. This requires that either 5 to 10 well volumes be removed or an indicator parameter should be monitored during the flushing process. Sampling devices should be totally inert, should not allow loss of volatiles, and should not expose the sample to oxygen. These requirements lead the author to recommend bailers, bladder pumps, or air driven piston pumps. Although cheaper or simpler devices can often be used, the potential liabilities of sampling are often so great that one should consider using the device or procedure which is subject to the least criticism rather than the minimum that appears to be technically justifiable.

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Soil Moisture Monitoring and Sampling Probe for Underground Storage Tanks and Surface Impoundments

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ABSTRACT: A review of available technologies for monitoring leaks from underground storage tanks and surface impoundments was performed to identify equipment that was most suited for this purpose. A single probe that combines the functions of a tensiometer and lysimeter was selected for additional research based upon this review. The unit detects changes in matric potential when functioning as a tensiometer and can also collect soil pore-water samples as a lysimeter. The probe developed from this effort was instrumented for both manual or remote monitoring, recording, and sampling. Instrumentation for automated maintenance allowed the unit to operate for extended periods of time without refilling the tensiometer mode of the probe with liquid.

Probe density depends upon soil texture and moisture content, geometry of the containment structure, and depth of installation. Calculations for determining the optimum probe placement based upon the diameter of the porous ceramic portion along with soil dispersion characteristics determine the primary variables for determining the optimum number of probes for a given containment structure. Probe sensitivity is controlled by the porous surface to vessel liquid volume, the radius of the porous section, and type of surface instrumentation.

KEY WORDS: tensiometers, lysimeters, monitoring, soil pore water sampling, surface impoundments, underground tanks, sampling probe

Indirect and direct moisture detection monitoring technologies were reviewed to assess their ability to provide a reliable and long-term method for detection and verification of leakage from surface impoundments and under-

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ground storage tanks. This review included indirect techniques, such as tensiometers [*1–3*], soil moisture blocks [*4,5*], capacitance sensors [*6,7*], thermocouple psychrometers [*8,9*] electrothermal probes [*10*], resistivity techniques [*11,12*], time domain reflectometry [*13,14*], and penetrometers [*15,16*]. Verification approaches of a leak through soil pore-water sampling included soil core extraction [*17,18*], pan lysimeters [*19,20*], and vacuum pressure lysimeters [*21*]. Vapor sampling techniques were also examined [*22–24*].

Review of this literature suggested that an automated device that relied upon soil moisture flux as an indicator of leakage would provide the optimum combination of detection functions. A system was therefore designed to (1) reduce the probability of incorrectly interpreting a leak signal, (2) reduce the reliance upon drilling for leak verification, (3) allow all functions to be electronically automated and accessed, and (4) be constructed of materials that provide long-term sensor integrity and performance. These detection functions were demonstrated in the use of the probe under surface impoundments containing hazardous wastes [*25*] and in a fly ash disposal pile [*26*].

Design and Operation

The major subsurface component of the monitoring system is a cylindrical vessel with a central tube of porous ceramic. The probe is filled with deaired water and allowed to function as a tensiometer to detect changes in the moisture content (matric potential) of the soil. In a saturated soil, the tensiometer will record a value greater than zero. As the soil dries, water within the tensiometer flows through the porous ceramic and into the soil in an attempt to maintain equilibrium with the soil pore water. Fluid movement from the vessel into the soil therefore results in a negative reading. Fluctuations between zero and negative values can be calibrated to changes in soil moisture. When an increase in soil moisture content indicates a possible leak, the liquid within the probe is evacuated and a vacuum is applied to collect a soil pore-water sample. The probe therefore functions as a lysimeter for soil water collection. The collected sample is used to verify whether the increasing moisture content indicated by the tensiometer is due to tank or surface impoundment leakage or is an artifact (for example, rainfall, spillage, and so forth). The use of porous ceramic precludes the use of the water sample collected in the probe for any use other than as a qualitative indicator to determine whether a particular liquid is present in the soil.

The probe can also be used for soil gas sampling. In order to use the probe for this purpose, a vacuum slightly higher than the bubbling pressure of the porous ceramic is applied. Soil gas can then be collected at the surface in an appropriate container. Since the probe and associated tubing are a closed system, only the soil gas entering the porous ceramic is retrieved.

The probe in Fig. 1 consists of a 16.5- by 5-cm wide cylinder with a 7.1-cm

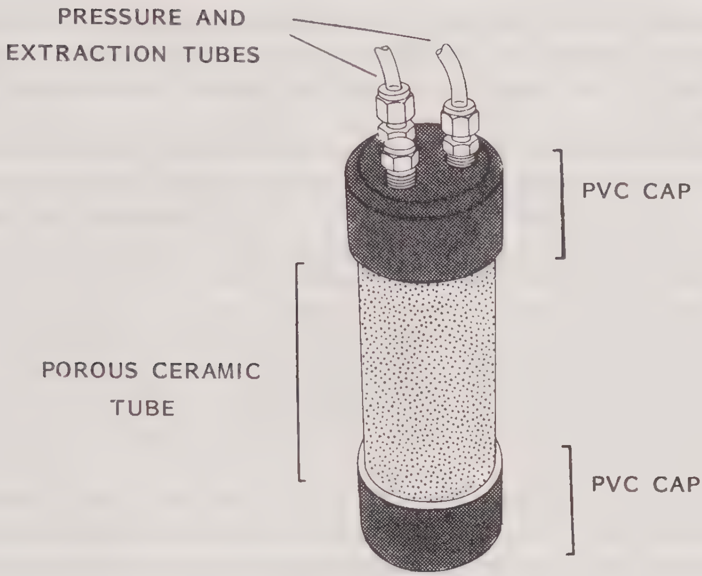

FIG. 1—*Tensiometer/lysimeter probe.*

ceramic tube positioned in the center of the cylinder. The large diameter and surface area of the ceramic significantly increases the sampling of the area and sample volume as compared to smaller units. The ceramic that was tested had a bubbling pressure equal to 850 MPa (85 centibar) ($\pm 0.05\%$), although bubbling pressures up to 125 kPa (1.25 bar) are available [*27*]. The use of conductance rather than bubbling pressure is recommended, however, as a more appropriate measure of the ability of the ceramic to conduct a fluid when performing as a tensiometer or as a lysimeter. Conductance is defined as the volume of pure water which in 1 min passes through the porous tube at 20°C when there is a pressure difference of one 100 kPa (1 bar) [*28*]. The integrity of the system is maintained by vacuum tight fittings and nylon tubing with a low diffusion coefficient.

Since unit sensitivity to changes in moisture content is a function of the porous area of the ceramic to liquid in the vessel, the probe was designed to accommodate an internal solid core [*29*]. The size of the core can be varied in order to displace various amounts of liquid in the vessel. Inclusion of the core allows the tensiometer mode of the vessel to be more sensitive to changes in soil moisture content.

Unit sensitivity of the tensiometer mode of the probe is also a function of the amount of dissolved air that enters the vessel through the porous ceramic over time. If a significant amount of air enters the probe, it will fail. This phenomenon is especially pronounced when the soil moisture decreases be-

yond the 100 kPa (1 bar) range. The normal procedure in such cases is to circulate new fluid into the probe and associated tubing with a peristaltic pump. For dry soils, the addition of tensiometer fluid may be required on a bi-weekly basis.

In order to reduce the labor intensive procedure of fluid circulation, instrumentation was designed to automatically recirculate liquid from a surface reservoir at prescribed intervals. A schematic of this arrangement is shown in Fig. 2. The surface instrumentation required for self-maintenance consists of a recirculation pump, an electrically operated valve, and an adjustable control module, which governs the maintenance frequency. The central manifold contains a temperature compensated transducer, which measures changes in soil suction. Power for this equipment may be trickle charged into a 12 V DC battery or from a solar panel at remote locations. The frequency of maintenance can be varied with intervals of up to 42 days. The duration of cycling can also be varied from 0 to 16 min. A network of probes used for monitoring moisture changes in a fly ash disposal site was cycled weekly, which appeared to be adequate in order to maintain the probe at maximum unit sensitivity.

A variety of installation approaches for new and existing containment facilities are available. Slant drilling with a hollow stem auger works well for existing tanks or smaller surface impoundments. Conventional drilling approaches are appropriate for new tanks/surface impoundments. A backfill

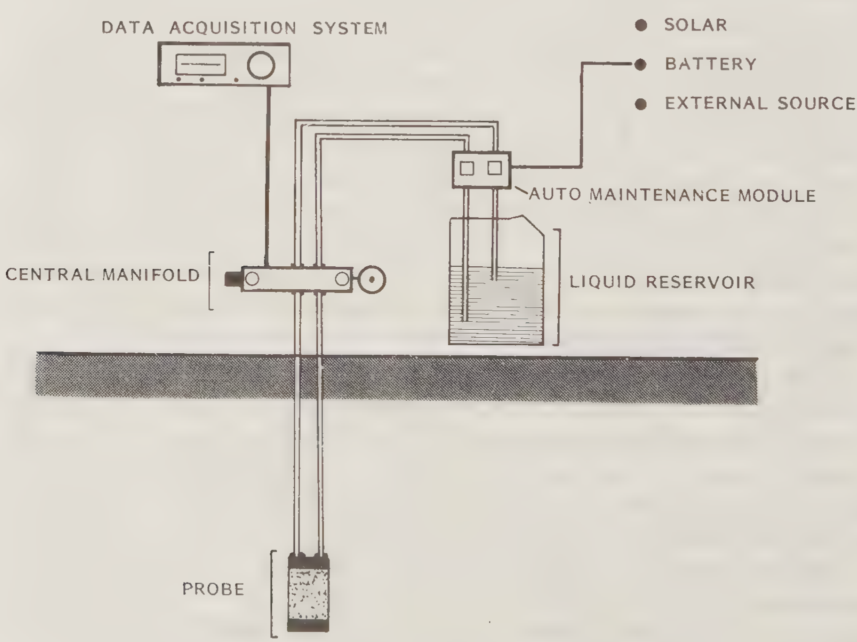

FIG. 2—*Schematic of automatic maintenance and recording system.*

material with a grain size of 0.0032 cm is optimal for increasing the radius of influence of the lysimeter portion of the probe. This backfill material, however, has the opposite effect when in the tensiometer mode by reducing the response time to soil moisture changes. Finer grained backfill will cause excessive fluid loss from the tensiometer with subsequent system failure.

The successful operation of the tensiometer/lysimeter probe is predicated upon four operational criteria:

(1) the ambient soil matric potential is less than 125 kPa (1.25 bar) for most of the year,

(2) the vessel, tubing, and instruments provide a closed system,

(3) the appropriate soil is available (for example, coarse gravels or clays significantly reduce unit performance), and

(4) the stored liquid should be of a compatible polarity as the tensiometer fluid.

The second criteria is the most critical to unit performance in an operational context, since accumulated air within the vessel reduces unit sensitivity and will eventually result in failure unless the air is removed. Air entry through the tubing is minimized with materials that have low gas diffusion coefficients.

Since the tensiometer function of the probe responds to changes in soil moisture content, the leakage of a nonpolar fluid will not be detected unless the soil is wet enough where displacement of the soil moisture by the nonpolar fluid occurs. Under dry soil conditions in which moisture displacement is not significant, three potential remedies exist to enable the probe to detect the leak. These are (1) to combine the probe with vapor detection capabilities (assuming that the fluid is volatile) [*30*], (2) alter the polarity of the porous ceramic, or (3) adjust the tensiometer fluid so that it responds to nonpolar fluids. The addition of a low-viscosity silicone based solvent to the tensiometer fluid, for example, has been successfully tested for the third remedy.

Unit Density

The installation of the tensiometer/lysimeter probe requires determining the optimum unit density for a prescribed depth under a tank or surface impoundment. The information required or this determination includes:

(1) type of containment structure and liquid characteristics;
(2) average ambient soil moisture conditions for most of the year;
(3) soil texture;
(4) approximate liquid dispersion characteristics of the soil; and
(5) radius of sampling influence.

The first two considerations will determine whether the detection probe is appropriate for these specific conditions. Probe density is determined by accounting for the expected dispersion characteristics within the backfill of the

containment structure and the native soil along with the radius of probe influence.

Since the measurement of dispersion characteristics of a soil is a complex process, approximate values based upon the soil type are used. Most values range from between a 1:1 to 1:3 ratio of depth to lateral dispersion [*31*]. Many underground tanks and surface impoundments are backfilled with fine to medium sand, which also contributes to liquid dispersion before entry into the native soil. By accounting for the expected backfill and the undisturbed soil dispersion values, a conservative dispersion value of the liquid at a certain depth can be approximated. Combining this information with the radius of influence of the detection probe will provide the optimum number of units for a certain depth below the surface impoundment or underground tank.

The radius of influence for the probe can be approximated given the following assumptions:

- Unsaturated hydraulic conductivity is $K = K_o \exp \alpha h$, where K_o and α are soil dependent, empirical constants [*32,33*] and h represents the pressure head.
- Matrix flux potential $\phi = K_o/\alpha[e^{\alpha h} - e^{\alpha h_o}]$

where

the steady state flow equation is $\nabla^2\phi - a(\partial\phi/\partial Z) = 0$,
h_o = constant pressure head at which $\phi = 0$, and the
$-Z$ axis is positive for vertical direction.

- Dimensionless variables in terms of actual variables:

if r_o is the porous tube radius, then $R_o = \alpha r_o$ and, if r is the distance from the center of the porous tube, then

$$R = \alpha Z/2$$

If Z is the depth coordinate, then $Z = (\alpha Z/2)$.

- Solution of $\nabla^2\phi - \alpha(\partial\phi/\partial Z) = 0$ for point sinks in dimension variables

$$\phi(R,Z) = \frac{K_o}{\alpha}[e^{\alpha h_1} - e^{\alpha h_o}]\left[1 - \frac{R_o}{\sqrt{R^2 + Z^2}}e^{(Z - \sqrt{Z^2 + R^2} + R_o)}\right]$$

- Steady state flow (cm^3/s) is

$$q = \frac{8\pi R_o K_o}{\alpha^2}e^{R_o}(e^{\alpha h_1} - e^{\alpha h_o})$$

These relationships assume a homogeneous, monodisperse soil and fluid, constant fluid density throughout the soil, no resistance to flow through the porous ceramic, no soil water interactions, and negligible effects from molec-

ular diffusion. Given these assumptions, the solution for unsaturated conductivity is in the form of [34]

$$K = K_o \exp(\alpha h)$$

$$= \alpha\phi + K_o \exp(\alpha h_o)$$

Detailed derivations based upon these relationships are available in the literature [35,36]. These solutions allow the maximum radial distance of R_M for a probe $\psi/q = 1$ as Z approaches $-\infty$ to be

$$R_M = [\alpha^2 q/4 K_o \exp(\alpha h_1)]^{1/2}$$

or by using q in

$$R_M = [2R_o \exp(R_o)]^{1/2} \{1 - \exp[\alpha(h_o - h_1)]\}$$

and

$$r_M = (2R_M/\alpha)$$

where

r_M = the maximum radius of influence of a lysimeter or tensiometer, cm,
r_o = radius of the porous ceramic tube of the probe, cm,
$h = h_o - h_1$,
h_1 = suction head at R_M in centibars,
h_o = suction head at the middle of the tensiometer tube in centibars. Not to exceed the bubbling pressure of the ceramic,
K_o = saturated hydraulic conductivity of the soil,
q = steady state flow rate for a tensiometer at infinite depth, cm^3/s,
α = empirically derived soil constant, cm^{-1}, as a measure of the relative importance of gravity and capillarity for a specific soil, and
ψ/q = the normalized Stokes stream function described by

$$[4\pi K_o \exp(\alpha h_1)/(\alpha^2 q)]R^2 + (1/2)[1 + (Z/\rho)\exp(Z - \rho)]$$

where

$R = \alpha r/2$,
$Z = \alpha z/2$, and
$\rho^2 = R^2 + Z^2$.

which is appropriate for all values of Z.

If compensation for dispersion effects of the liquid leaking from the tank or

surface impoundment is not included then the radius of the sampling influence considered is a function primarily of r_o, $(h_1 - h_o)$, and α. The radius of influence is therefore optimized in a fine textured soil and with a porous section with a large radius r_o. Incorporating this information with the dispersion characteristics of a particular soil and liquid provides the data for specifying sensor density at a particular depth. While sensor installation at greater depths will result in reduced sensor density, this reduction must be balanced by the increased response time of the monitoring system to a leak.

Conclusions

The development of the tensiometer/lysimeter probe provides a long-term sensing device for use under new or existing surface impoundments or buried tanks. The probe offers a variety of instrumentation approaches from a manual to a fully automated recording and maintenance system. Surface instrumentation is available which can provide automatic refilling of the tensiometer fluid for extended periods of time.

Calculations performed for the determination of the radius of influence for the tensiometer and lysimeter modes of the probe indicate that soil moisture content, soil texture, and probe geometry are the primary variables controlling the radius of influence. When this information is combined with estimated values for the dispersion for the soil, the optimum number of probes at a given depth below the underground tank or surface impoundment can be approximated.

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Practices for Sampling Solid Wastes from Point Discharges and Impoundments

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ABSTRACT: Practices for sampling solid wastes from point discharges and impoundments are being developed for ASTM Committee D-34 on Waste Disposal and will provide guidance for obtaining representative samples of solid wastes from point discharges and surface impoundments. The sampling guidelines outline safety procedures, design considerations, sampling equipment, and sampling procedures. Proper design is a key component of any waste sampling program and is emphasized in these practices. The frequency of sampling or the spatial distribution of samples required to obtain a descriptive sample depends on the variability of the waste composition and the precision of waste analysis required. Given the waste variability and precision requirements, the number of samples necessary can be calculated using fundamental statistical concepts.

KEY WORDS: wastes, sampling, solid waste sampling, sampling impoundments, sampling solid waste point discharges, sample variability, sampling design

The procedures outlined in this paper are guides for obtaining "descriptive" samples of solid, semi-solid, and liquid wastes from flowing streams and impoundments. They incorporate many of the same procedures and equipment described previously [*1*–*5*]. These guidelines by themselves will not necessarily result in the collection of samples representative of the total waste mass. The degree to which samples describe a waste mass must be estimated by application of appropriate statistical methods and measures of quality assurance.

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These practices provide guidance for obtaining samples of waste from discharge points such as pipes, sluiceways, conduits, and conveyor belts and from impoundments (ponds or lagoons). They do not address flow- and time-proportional samplers and other automatic sampling devices. For point discharges, samples are taken from a flowing waste stream or moving waste mass and, therefore, are descriptive only within a certain time period. The length of the time period for which a sample is descriptive will depend on the sampling frequency and compositing scheme. Likewise, samples are collected from impoundments at points selected at random. The number of samples collected over an area and with depth will determine the precision of the sampling.

Safety

In all sampling practices, safety should be the first consideration. Personnel involved in the sampling should be fully aware of, and take precautions against, the presence of toxic or corrosive gases, the potential for contact with toxic or corrosive liquids or solids, and the dangers of moving belts, conveyors, or other mechanical equipment. The following safety precautions are not comprehensive. Rather, they provide additional guidance on health and safety to complement professional judgment and experience.

The hazards of waste sampling can vary from immediately dangerous to life and health to nonhazardous. An experienced professional, knowledgeable about safety regulations and practices (Occupational Safety and Health Administration [OSHA], American National Standards Institute [ANSI], and the U.S. Environmental Protection Agency [EPA]), should make the decisions regarding the appropriate level of protection (for example, personal protective equipment) at the particular job site. All support concepts, such as rescue teams for work in immediately dangerous atmospheres, first aid, and location of the nearest health facility, must be determined before work begins.

Personnel should wear protective equipment when response activities involve known or suspected atmospheric contamination; when vapors, gases, or particulates may be generated; or when direct contact with skin-affecting substances may occur. Respirators primarily protect lungs; they also protect the gastrointestinal tract and eyes against air toxicants depending on the type selected. Chemical-resistant clothing can protect the skin from contact with skin-destructive and skin-absorbable chemicals. Good personal hygiene limits or prevents ingestion of material.

Equipment to protect the body against contact with known or anticipated chemical hazards can be divided into four categories according to the degree of protection afforded [*6*]:

- *Level A:* Should be worn when the highest level of respiratory, skin, and eye protection is needed.

• *Level B:* Should be selected when the highest level of respiratory protection is needed but a lesser level of skin protection. Level B protection is the minimum level recommended on initial site entries until the hazards have been further defined by on-site studies and appropriate personnel protection utilized.

• *Level C:* Should be selected when the type(s) of airborne substance(s) is known, the concentration(s) is measured, and the criteria for using air-purifying respirators are met.

• *Level D:* Should not be worn on any site with respiratory or skin hazards. It is primarily a work uniform providing minimal protection.

The Level of Protection selected should be based primarily on:

• Type(s) and measured concentration(s) of the chemical substance(s) in the ambient atmosphere and its toxicity.

• Potential or measured exposure to substances in air, splashes of liquids, or other direct contact with material caused by work being performed.

In situations where the type(s) of chemical(s), concentration(s), and possibilities of contact are not known, the appropriate level of protection must be selected based on professional experience and judgment until the hazards can be better characterized.

Figure 1 summarizes the types of protective clothing and equipment for various levels of hazard.

Protection	Self-contained breathing apparatus	Canister-equipped respirator	Fully encapsulating chemical-resistant suit	Chemical resistant clothing	Coveralls	Gloves	Gloves (inner)	Boots, outer, chemical resistant	Boots, steel toe	Hard hat (under suit)	Hard hat with face shield	Safety glasses	2-way radio communications
Level A	•		•			•	•		•	•			•
Level B	•			•	•	•	•	•	•		•		•
Level C		•		•	•	•	•	•	•		•		$\bullet^2$
Level D					•	•		$\bullet^2$	•		$\bullet^2$	•	

FIG. 1—*Summary of personnel protective equipment for solid waste sampling* [6]; 2 *is optional.*

Level A Protection

The fully encapsulating suit provides the highest degree of protection to skin, eyes, and respiratory system if the suit material is resistant to the chemical(s) of concern during the time the suit is worn or at the measured or anticipated concentrations. While Level A provides maximum protection, the suit material may be rapidly permeated and penetrated by certain chemicals from extremely high air concentrations, splashes, or immersion of boots or gloves in concentrated liquids or sludges. These limitations should be recognized when specifying the type of chemical-resistant garment. Whenever possible, the suit material should be matched with the substance it is used to protect against.

Many toxic substances are difficult to detect or measure in the field. When such substances (especially those readily absorbed by or destructive to the skin) are known or suspected to be present and personnel contact is unavoidable, Level A protection should be worn until more accurate information can be obtained.

Level B Protection

Level B equipment provides a high level of protection to the respiratory tract, but a somewhat lower level of protection to skin. The chemical-resistant clothing required in Level B is available in a wide variety of styles, materials, construction detail, permeability, and so forth. These factors all affect the degree of protection afforded. Therefore, a specialist should select the most effective chemical-resistant clothing (and fully encapsulating suit) based on the known or anticipated hazards and job function.

For initial site entry and reconnaissance at an open site, approaching whenever possible from the upwind direction, Level B protection (with good quality, hooded, chemical-resistant clothing) should protect response personnel, providing the conditions described in selecting Level A are known or judged to be absent.

Level C Protection

Level C protection is distinguished from Level B by the equipment used to protect the respiratory system, assuming the same type of chemical-resistant clothing is used. The main selection criterion for Level C is that conditions permit wearing air-purifying devices.

Total unidentified vapor/gas concentrations of 5 ppm above background require Level B protection. Only a qualified individual should select Level C (air-purifying respirators) protection for continual use in an unidentified vapor/gas concentration of background to 5 ppm above background. Level D protection is primarily a work uniform. It should be worn in areas where (1) only boots can be contaminated or (2) there are no inhalable toxic substances.

Sampling Design

The frequency of sampling and the number of composites required to obtain a sample of the waste will depend on the following:

- The time or spatial variability of the waste composition.
- The time span or spatial area that the sample is to represent.
- The precision of waste analysis that is required, for example, if a hazardous constituent is present in the waste at levels near the regulatory limit or another limit of concern, then greater precision will be required than if the levels are well below the limits of concern.

To obtain a descriptive sample of a waste, the concentration levels and approximate variation in the constituents of concern should first be estimated. In some cases, an estimate of the characteristics of a waste can be made based on knowledge of the processes that produce the waste. This method of designing a sampling strategy is commonly referred to as engineering judgment. It is often sufficient if the goal is simply to establish whether a waste meets some set criteria, such as Resource Conservation and Recovery Act (RCRA) hazardousness criteria. However, a more exacting approach to sampling design will be needed for wastes produced from complex and variable processes, or if a more precise description of the waste's average characteristics are required. A more exacting approach is described below.

For the sampling design, the time period or volume of the waste for which a composition estimate is desired must first be defined. If the time period or volume for which estimates are desired is not homogeneous, then suitable strata may be defined. Differences in level of contaminants and in variability of the contaminants may provide bases for stratification.

A sampling unit should be defined. This unit is the primary sampling unit (psu), which is selected at the first stage of the sampling within each stratum. Define a unit of time for the psu, for example, amount of discharge of effluent in 1, 5, 10 s, or whatever time unit is appropriate. Suppose the total period of interest is 1:00 PM to 6:00 PM for a given stratum, and 10 s of discharge forms a sampling unit. Then the total sampling period comprises $6 \times 60 \times 5 = 1500$ sampling units. As an example for simple random sampling, the sampler might need to take 5 psus. Random numbers when used could come up as 224, 1403, 286, 381, and 1099. During each of the 10-s intervals designated by these random numbers for the set of 1500 such intervals, one sample unit of material would be obtained at the discharge point.

Using the estimated sample composition and variance either from a pilot sampling effort or engineering judgment, the number of samples required to achieve the desired precision in waste composition can be estimated using fundamental statistical concepts, as follows (financial constraints not considered)

$$n = t_{0.80}^2 s^2/d^2 \tag{1}$$

where

n = appropriate number of samples to be collected;
$t^2_{0.80}$ = the square of the tabulated value of Student's t for a two-sided confidence interval and a coverage probability of 0.80 for the unknown mean, with the degrees of freedom defined for the s^2 used to estimate the population variance σ^2;
s^2 = a preliminary estimate of σ^2 obtained from previous samplings, a pilot sampling effort, or other information such as the likely range of the population values; and
d^2 = a deviation to be exceeded only in two cases out of ten in repeated sampling for the quantity $|\bar{X} - \mu|$, the difference in absolute value between the sample average and the population mean.

Although the use of Student's t distribution is based on an underlying normal distribution for the measurements, the robustness of the t statistic for many applications may be relied upon here. If ancillary information seems to indicate that normality may not be a good assumption, then a goodness of fit test (for example, the Lilliefors test) should be performed to determine if the assumption of a normal distribution is reasonable. If the goodness of fit test, such as the Lilliefors, shows the contention of normality is acceptable, it does not mean that the parent population is normal. But it does mean that the Student's t distribution does not appear to be an unreasonable approximation to the true unknown distribution. If the Lilliefors test shows that a normal distribution does not adequately fit the data, then further pilot sampling will be required to adequately determine the temporal distributions at the discharge point.

The following hypothetical example illustrates the use of Formula 1:

1. A preliminary study of barium levels in sludge collected from a discharge pipe generated values of 86, 90, 98, and 104 ppm for barium in four sludge samples. Based on these values and a knowledge of the processes producing the waste, the sludge is judged to be a continuous, homogeneous stream. Therefore, preliminary estimates of sample average $\bar{X}$ and sample variance s^2 are calculated as

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n} = \frac{86 + 90 + 98 + 104}{4} = 94.50,$$

and

$$s^2 = \frac{\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2 \Big/ n}{n - 1} = \frac{35\,916.00 - 35\,721.00}{3} = 65.00$$

2. The deviation not to be exceeded for measured barium in the sludge samples d is chosen as 5.50 ppm, that is, the difference between the sample average and the population mean should not exceed 5.50 ppm at the 80% confidence level

$$d = |\bar{X} - \mu| = |94.50 - 100.0| = 5.50$$

3. The value of $t_{0.80}$ is obtained from tabulated values of Student's t, as

TABLE 1—*Tabulated values of Student's* t *for evaluating solid wastes.*

Degrees of Freedom $(n - 1)$[a]	Tabulated t Value[b]
1	3.078
2	1.886
3	1.638
4	1.533
5	1.476
6	1.440
7	1.415
8	1.397
9	1.383
10	1.372
11	1.363
12	1.356
13	1.350
14	1.345
15	1.341
16	1.337
17	1.333
18	1.330
19	1.328
20	1.325
21	1.323
22	1.321
23	1.319
24	1.318
25	1.316
26	1.315
27	1.314
28	1.313
29	1.311
30	1.310
40	1.303
60	1.296
120	1.289
∞	1.282

[a]Degrees of freedom df are equal to the number of samples n collected from a solid waste less one.

[b]Tabulated t values are for a two-tailed confidence interval and a probability of 0.80 (the same values are applicable to a one-tailed confidence interval and a probability of 0.90).

shown in Table 1. Although an assumption of a t distribution would seem to be restrictive, it can be shown that even nonnormal populations possessing bell-shaped distributions can be closely approximated by a t distribution. From the preliminary study $n = 4$, and the degrees of freedom, $n - 1$, n is 3. Therefore

$$t_{0.80} = 1.638$$

4. The appropriate number of sludge samples to be collected from the discharge pipe is

$$n = t_{0.80}^2 s^2/d^2 = \frac{(1.638^2)(65.00)}{5.50^2} = 5.77$$

or six. That number of samples (plus extra for protection against poor preliminary estimates of $\bar{X}$ and s^2) is collected from the pipe by a simple random process.

The use of statistical techniques to estimate the level of confidence that samples collected will fall within is important for evaluation of all data associated with sampling. Quality assurance should be developed in the sampling plan to identify the assumptions used in design of the sampling strategy, in particular, those assumptions for obtaining a descriptive sample of a waste. Such documentation is critical for evaluation of the sampling plan, as well as for evaluation of data gathered by other sampling episodes at the same location. At the least, the quality assurance plan should include the following:

- Sample handling quality control by carrying a quality control (QC) sample of known concentration through all of the sampling and analytical steps and
- Analytical quality control with duplicate analyses, spike recovery, and analysis of certified standards. Most analytical laboratories should have their own internal quality control procedures.

More rigorous quality control/quality assurance procedures may be required depending on the particular goals of the sampling program (for further information see Ref 5).

Sampling Equipment and Procedures

The types of sampling equipment best for a given situation can vary almost as much as the impoundments and discharges themselves. Often sampling equipment must be modified and improvised on-site to meet the needs of the situation. A few of the more standard types of solid waste sampling equipment and the procedures for their use are presented below.

Equipment

Pond or Dipper Sampler—The sampler consists of a glass, plastic, or other nonreactive beaker clamped to the end of a two- or three-piece telescoping aluminum or fiberglass pole that serves as the handle. This sampler is for liquids and free-flowing slurries. It can be used as far as 3.5 m (11.5 ft) from the bank.

These samplers are not available commercially and must be fabricated to conform to the specifications detailed in Fig. 2. Table 2 lists the parts required to fabricate a dipper.

Trier Sampler—A trier consists of a tube cut in half lengthwise with a sharpened tip that allows the sampler to cut into sticky solids and loose soil. A trier samples moist or sticky solids with a particle diameter less than 1/2 the diameter of the trier.

Triers 61 to 100 cm long and 1.27 to 2.54 cm in diameter, as shown in Fig. 3, are available at laboratory supply stores. A larger trier can be fabricated.

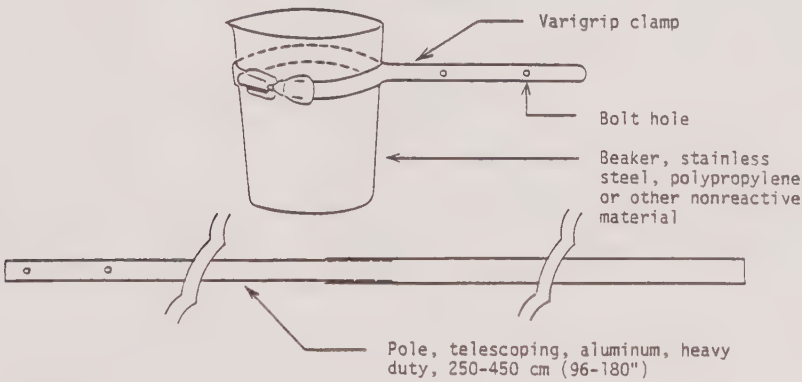

FIG. 2—*Dipper sampler* [5].

TABLE 2—*Parts for constructing a pond or dipper sampler.*[a]

Quantity	Item	Supplier
1	adjustable clamp, 6.4 to 8.9 cm (2 1/2 to 3 1/2 in.) for 250 to 600 mL beakers; heavy duty aluminum	laboratory supply houses
1	tube 2.5 to 4.5 m long with joint cam locking mechanism; diameter 2.54 cm ID and 3.18 cm ID	swimming pool supply houses
1	polypropylene or glass beaker, 250 to 600 mL	laboratory supply houses
4	bolts 2 1/4 by 1/4 in., NC	hardware stores
4	nuts, 1/4 in., NC	hardware stores

[a]NOTE: ID is inside diameter, 1 in. = 2.54 cm, and NC is national coarse.

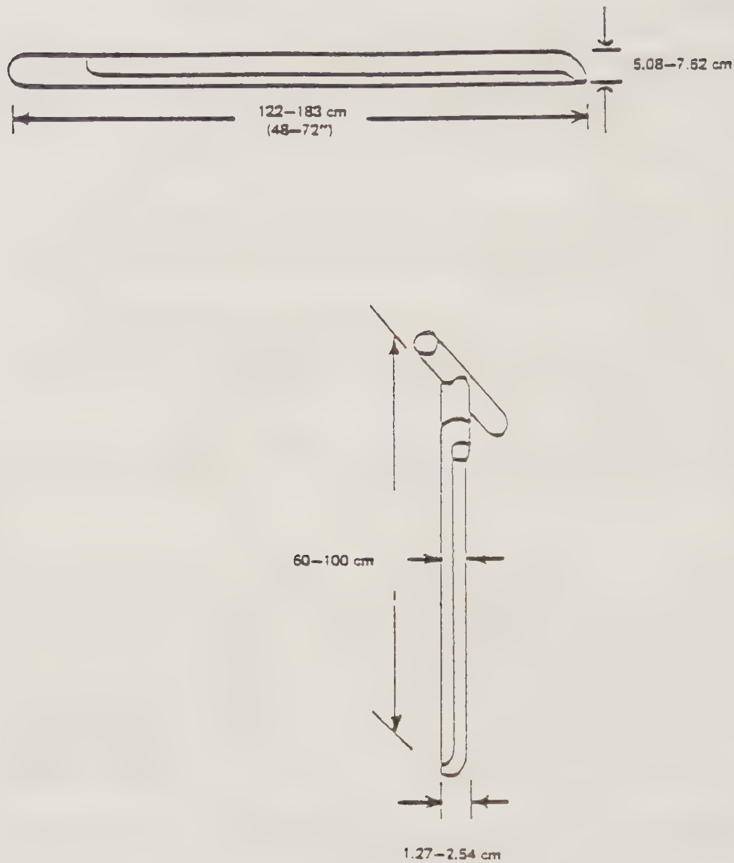

FIG. 3—*Sampling triers* [5].

Thief—A thief consists of two slotted concentric tubes usually made of stainless steel or brass (Fig. 4). The outer tube has a conical pointed tip that permits the sampler to penetrate the material being sampled. The inner tube is rotated to open and close the sampler. A thief is used to sample dry granules or powdered wastes whose particle diameter is less than $^1/_3$ the width of the slots. A thief is available at laboratory supply stores.

Scoop or Shovel Sampler—For solid or solid-like discharges from belts, a scoop or shovel should be used. Where routine sampling is to be performed, a scoop may be designed to match the width and contour of the belt. In this way, a single time increment sample may be taken in one scoop.

A scoop or shovel may also be used for obtaining samples of solid or solid-like waste from impoundments.

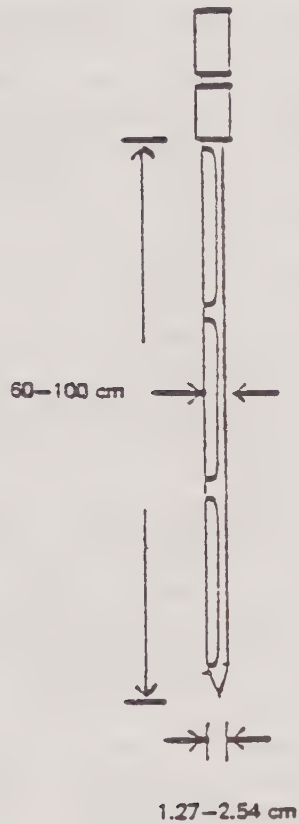

FIG. 4—*Thief sampler* [5].

Sampling Procedure

All sampling equipment must be cleaned before use, and if possible, it is preferable to have them lab cleaned. Improper cleaning will cause cross-contamination of samples. Disposable samplers are a very simple way of eliminating the cleaning problem. When samplers are lab cleaned, it is equally important that the samples be protected from contamination by wrapping, packaging, or containerizing in clean noncontaminating material.

Equipment cleaned in the lab should be washed with a warm detergent solution, rinsed several times with tap water, rinsed with deionized water, and air dried. If organic analyses are to be run, wash with a warm detergent solution (it may first be necessary to wipe with an absorbent cloth to eliminate residues), rinse several times with tap water, rinse with deionized water, rinse

with an appropriate organic solvent (the solvent should be, if possible, the extracting solvent), and oven dry at 105°C for at least 1 h.

Cleaning procedures in the field are the same except that tap water rinses and solvent rinses may not be practical. The user must be careful in using a solvent rinse without oven drying as it may permeate other samples if shipped in the same container or it may react with constituents in the waste. It should be kept in mind that field cleaning requires the capability to carry a large amount of water.

The volume of sample required will vary with the intended analyses, but in most cases 1000 mL (1 qt) is sufficient.

Sampling Liquids or Slurries with a Dipper Sampler—Assemble sampler by bolting adjustable clamp to pole. Place beaker in clamp and fasten shut. Turn sampler so the mouth of beaker faces down and insert into waste. Turn beaker right side up when dipper is at desired depth. Allow beaker to fill completely as shown by cessation of air bubbles. Raise dipper and transfer sample to container.

Sampling Moist Solids with a Trier Sampler—Insert trier into waste material 0° to 45° from horizontal. Rotate trier to cut core of the waste. Remove trier with concave side up and transfer sample to container.

Sampling Dry Granular Solids with a Thief Sampler—Insert closed thief into waste material. Rotate inner tube to open thief. Wiggle the unit to encourage material to flow into thief. Close thief and withdraw. Place sampler thief in a horizontal position with the slots facing upward. Remove inner tube from thief and transfer sample to a container.

Sampling Liquid Discharges with a Dipper Sampler—Pass the dipper in one sweeping motion through the discharge stream at a rate such that the dipper is filled in one pass. Make enough passes to cover the entire cross-sectional area of the discharge stream.

Sampling Granular Discharges with a Scoop or Shovel—Clean the scoop or shovel as appropriate for the desired chemical analysis to prevent cross-contamination. In some cases, it may be necessary to dedicate equipment to specific waste types or waste strata. Sample at a convenient point along the belt. Sample the waste with the scoop or shovel making sure to sample across the entire width of the belt. Be sure all fines and any liquid are also included in the scooped sample.

Sample Containers

Plastic, glass, or other nonreactive containers should be used. Plastic should be used for wastes that are to be analyzed for metals and for wastes containing strong alkali and hydrofluoric acid. Glass containers are preferred for wastes to be analyzed for organics. High-density or linear polyethylene plastic containers offer the best combinations of chemical resistance and low

cost. Soda glass containers are recommended because of their low cost and availability.

The containers should have wide mouths with tight, screw-type lids. Teflon® cap liners with rigid plastic screw caps should be used with glass containers. The sizes should be 1000 to 2000 mL (1 qt to 1/2 gal).

Compositing samples are often necessary in order to obtain an average sample, descriptive of a given area of waste or a given time period of waste discharge. However, the sampler should be aware of stratification in the waste or any inhomogeneities before compositing samples. Compositing samples of waste from different strata (that is, different composition) may not result in a sample that is descriptive of the waste body.

If compositing of samples is to be performed it is sometimes necessary to have the laboratory mix the sample. Depending on the type of analysis to be conducted, drying the sample or slurrying with distilled water may be possible in the laboratory to facilitate mixing. The laboratory personnel are often better equipped to make such decisions and determine what effect such procedures would have on the analysis. If the composite has not been appropriately mixed before shipment, this should be clearly indicated on the sample.

Preservation techniques appropriate for the analyses or testing to be conducted should be used. For most solid wastes preservation consists of sealing in a container and storing at 4°C until analysis.

Sample Labeling and Shipping

An indelible label should be secured to the container identifying the sample. The label should contain or reference the following information:

- Name and location of site.
- Date and time of sampling.
- Location of sampling.
- Sample number.
- Description and disposition of sample.
- Name of sampling personnel.
- Full weight of sample and container upon shipping.
- Type of preservative.
- Analytical requirements.

Pack the sample container securely in a shipping container. If the sample is to be analyzed for volatile organics it should be packed in ice and cooled to 4°C. A min-max thermometer should be packed with the sample container. It may be desirable to pack all samples in ice to retard degradation. However, the physical condition of some samples, such as oil-water emulsions, may be altered by cooling. Follow Department of Transportation (DOT) shipping regulations. Make arrangements for handling, logging in, adequate storage

and analysis of the sample at its destination. If warranted, follow chain of custody protocol.

Summary

Even the simplest of sampling events should include sufficient planning for the following:

- Safety; the first consideration.
- Design of sampling; this may be based on engineering knowledge of the processes producing the waste. For more precision in sample collection, a statistical sampling design is needed. This requires some prior knowledge of the concentrations of the constituents of concern in the waste and their variability.
- Knowledge of sampling equipment and procedures, available in ASTM or EPA published documents.
- Sample logistics, including types of containers, and methods of labeling and shipping.

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ASTM Standard Leach Test D 3986: A History*

REFERENCE: Jackson, K., **"ASTM Standard Leach Test D 3986: A History,"** *Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume, ASTM STP 933*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986, pp. 367–374.

ABSTRACT: In 1977 ASTM Subcommittee D19.12 (currently ASTM Committee D-34 on Waste Disposal) was organized to develop standard test methods for the evaluation of hazardous waste. A standard leach test was the first test that needed to be identified. The development of this standard leach test involved a two phase testing program. The phase one testing program included 21 laboratories testing six waste streams for three parameters. The phase one program identified the areas in the proposed test method that were responsible for the very high variability found during the testing program. The second phase testing program was designed and carried out to address those areas of variability. The proposed test method was adopted as a standard in June 1980.

KEY WORDS: leaching, analyzing, extraction, leachate, leach test

ASTM Subcommittee D19.12 (currently ASTM Committee D-34 on Waste Disposal) was formed in 1977 to address the absence of standard test methods for the evaluation of hazardous wastes. The first test that needed to be identified was a standard test for evaluating the leaching potential of a solid waste. The U.S. Environmental Protection Agency (EPA) was in the process of developing a procedure of this type to be used in the implementation of the Resource Conservation and Recovery Act (RCRA). The subcommittee first evaluated those methods under consideration by the EPA and determined them to be technically unsuitable for their intended purposes and therefore found it necessary to develop their own test method. This new method would then undergo extensive intralaboratory testing to prove that it was indeed a standard method. In conjunction with these tests, the EPA's Toxicant Extraction Procedure (TEP) would be further evaluated.

*From ASTM Method for Shake Extraction of Solid Wastes with Water (D 3987).

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The subcommittee decided to develop two types of leach tests. One would utilize distilled water as the leaching median (Method A) and the other would use an acetate buffered media (Method B). The initial drafts of the two procedures were distributed to the participating laboratories in Feb. 1977.

In its final stage, Phase 1 included six different wastes (fly ash, American Petroleum Institute [API] separator sludge, scrubber sludge, metal finishing, textile, and soil). The testing design was as follows: three replicate extractions of each waste, utilizing both ASTM methods and the EPA TEP procedure. Twenty one laboratories were to carry out the leaching tests and analyze the leachate for three parameters: pH, calcium, and iron.

Phase I

The initial program included the following:

3 = 3 methods each lab (ASTM "A", ASTM "B", and EPA "TEP"),
18 = 6 wastes, three replicates each waste,
6 = 3 parameters determined in duplicate (pH, calcium, and iron),
21 = laboratories, and
6804 = total number of determinations.

This initial program had to be trimmed down to include only five labs testing all of the six waste materials, and the remaining labs were required to test no more than three of the wastes. The laboratory results were sent to an engineering group where the data were subjected to statistical analysis. The statistical analysis showed the overall precision to be highly variable. The greatest variability being between laboratories; however, single operator precision was also unacceptable. It was concluded that the following factors may have contributed to the very poor precision results:

1. *Sampling Procedures*—Sample collection was the responsibility of the waste supplier. While general sampling guidelines were discussed, no specific procedures were required.

2. *Waste Transport*—Waste suppliers were to choose their sample containers and method of transporting to the testing laboratory. Labeling was also the responsibility of the waste supplier.

3. *Sample Storage and Preservation*—Samples stored by the participating laboratories were subject to the environmental conditions of the specific lab. Procedures for sample preservation were delineated in each of the analytical procedures; however, several laboratories deviated from these procedures.

4. *Testing Time Period*—Although certain checks and requirements were placed on testing laboratories, the testing program was significantly extended. Differing test data on the textile waste and metal finishing waste was especially seen between labs testing these materials at the initiation and termination of the testing.

5. Several laboratories did not strictly adhere to the requirements of Methods A and B. The following exceptions were noted:

Lab 16—use of a shaker with 89 7.6-cm cycles/min (3-in. cycles/min); samples were roll-blended for 45 min.

Lab 8—extract used for iron determination was acidified with nitric acid (HNO_3) instead of hydrochloric acid (HCl).

Lab 14—extract used for iron determination was acidified with 1 mL-HCl/100 mL extract.

Lab 22—calcium determined by inductively coupled argon plasma spectrophotometer (ICAP) analysis.

Lab 5—rotating shaker used.

Lab 19—shaking rate of 120 to 130 strokes/min used.

6. *Matrix Effect of Wastes*—Analytical methods used to evaluate the leachate extraction procedures were designed for the analysis of waters from lakes and streams. The very complex matrix of waste materials can lead to a high degree of variability when using these test methods.

7. *Selection of Analytical Methods*—Certain misunderstanding surfaced regarding the selection of the appropriate option for a specific analytical procedure.

8. No qualification samples were analyzed by the participating laboratories to determine their ability to perform the required analysis.

9. The waste samples used were not uniform.

10. Containers used for the leach testing were of different size, and materials of construction also differed.

Phase I data evaluation was completed in Dec. 1978, and the results given to subcommittee members. The subcommittee's review of Phase I data established the need for a Phase II program; this program would be designed to eliminate the areas of variability that had been identified in the Phase I program.

Phase II

In Jan. 1979, two years after the subcommittee was formed, the Phase II testing program was initiated. In order to eliminate the testing variables identified in Phase I, the following procedures were incorporated into the Phase II program:

1. All the laboratories were first required to analyze a quality control sample provided by the EPA. This step would provide information about the laboratories' analytical capability.
2. All metal analyses were to be conducted using atomic absorption graphite furnace techniques using the EPA methodology.
3. Standard sample bottles were required.

4. Standard extraction equipment was required.
5. Extractor speed was specified.
6. A standard waste sample was prepared.
7. Sampling guidelines for all wastes were established.
8. National Bureau of Standards (NBS) personnel were called on to assist in program design and implementation.

Once the program design had been established and approved by the subcommittee members, the next step was the collection of the wastes to be used.

The wastes selected for Phase II testing are shown in Table 1. One of these wastes (Sample 9), a bituminous coal fly ash from Pennsylvania, was selected to be processed as a standard waste. This effort began in Sept. 1979 with the collection of 817 kg (1800 lb) of fly ash from the plant; 544 kg (1200 lb) of the ash was screened and blended, then emptied into 29 23-L (6-gal) containers. A total of 2000 samples were then prepared by weighing 100 g or 350 g or both of fly ash into standard sample containers. These were then divided into a representative subset of samples to be analyzed to determine sample heterogeneity. Analysis of this data proved the fly ash sample to be extremely uniform and suitable for use as a "standard fly ash."

The laboratories were required to analyze the EPA quality control samples, and the data were statistically examined before they were sent to be waste samples. The results of that examination are shown in Tables 2 and 3. The elements exhibiting the largest standard deviation were barium, lead, and arsenic. Of the 15 labs that ran the quality control (QC) samples, two were

TABLE 1—*Phase II—wastes.*

Sample	Material	Source
1	retorted oil shale	Colorado
2	raw oil shale	Michigan
3	retorted oil shale	Michigan
4	raw oil shale	Morocco
5	retorted oil shale	Michigan
6	fluidized bed combustion residue	Virginia
7	fluidized bed combustion residue	Virginia
8	fluidized combustion residue	Ohio
9	bituminous coal fly ash	Pennsylvania
10	bituminous coal fly ash	Virginia
11	bituminous coal fly ash	West Virginia
12	bituminous coal bottom ash	West Virginia
13	bituminous coal boiler slag	West Virginia
14	lignite fly ash	North Dakota
15	lignite scrubber sludge	North Dakota
16	magnetohydrodynamic slag	Tennessee
17	subbituminous coal fly ash	Illinois
18	bituminous coal scrubber sludge	Pennsylvania
19	bituminous coal scrubber sludge	Pennsylvania

TABLE 2—*Phase II: EPA quality control sample results (all results in μg/L).*

Sample	True Value	Laboratory 1	2	3	4	5	6	7	9	10	11	12	13	14	15	16	17	18	19	$\bar{X}$	S
As																					
1	29.4			32.		22.	20.	9.		28.	24.	26.		26.	36.	45.[b]	...	42	28.	24.3	7.31
2	48.2			49.		33.	58.	37.		45.	39.	40.		42.	53.	110[b]	...	56	16.	40.3	12.02
Ba																					
1	334.0			...		360.	320.	300.		263.	530.[b]	368.		300.	330.	400.	296.	...	230.	316.7	50.57
2	602.0			...		590.	520.	540.		497.	734.[b]	636.		520.	480.	400.	532.	...	550.	526.5	63.16
Cd																					
1	4.4			4.5		<2.	17.[b]	3.9		<10.	3.8	4.		5.2	7.	7.	4.8	3.	4.	4.64	1.82
2	12.0			10.		20.	32.[b]	10.		<10.	11.	11.		18.	12.	18.	11.	9.	9.	12.8	4.89
Cr																					
1	26.6			24.		30.	25.	20.		23.	20.	31.		27.	32.	25.	24.	31.	30.	26.1	4.25
2	44.0	NA[a]	NA	40.	NA	40.	52.	40.	NA	46.	32.	48.	NA	42.	50.	46.	42.	50.	50.	44.4	5.85
Pb																					
1	35.1			33.		20.	42.	<50.		16.	32.	36.		45.	36.	35.	17.	38.	30.	30.9	10.15
2	61.0			55.		70.	76.	59.		26.	51.	65.		96.	64.	54.	35.	72.	60.	59.7	19.97
Hg																					
1	1.4			...		9.4	1.5	<2.		0.7	1.2	1.2		2.0	0.7	1.	0.8	1.	0.5	1.06	0.443
2	3.2			...		7.0	6.0	<2.		1.3	2.2	2.2		1.3	1.4	2.	2.7	3.	1.2	2.13	1.47
Se																					
1	9.7			18.		7.0	10.	...		4.3	11.	6.		10.	11.	15.	...	...	11.	9.48	3.22
2	15.4			20.		11.	12.	...		8.2	17.	8.		17.	14.	20.	...	...	20.	14.1	4.64
Ag																					
1	28.5			22.		24.	35.	20.		24.	96.[b]	28.		34.	30.	38.	29.	23.	29.	29.1	5.53
2	48.2			34.		14.	50.	50.		43.	152.[b]	46.		46.	50.	64.	56.	40.	47.	46.6	12.92

[a]NA is not analyzed.
[b]Results eliminated for calculation of $\bar{X}$ and S.

TABLE 3—*Phase II: EPA quality control sample results (all results in ug/L).*

		Laboratory														
Sample	True Value	3	5	6	7	10	11	12	14	15	16	17	18	19	*X*	*S*
As																
1	29.4	32.	22.	20.	9.	28.	24.	26.	26.	36.	45.[a]	. . .	42.	28.	24.3	7.31
2	48.2	49.	33.	58.	37.	45.	39.	40.	42.	53.	110.[a]	. . .	56.	16.	40.3	12.02
Ba																
1	334.0	. . .	360.	320.	300.	263.	530.	368.	300.	330.	400.	296.	. . .	230.	316.7	50.57
2	602.0	. . .	590.	520.	540.	497.	734.[a]	636.	520.	480.	400.	532.	. . .	550.	526.5	63.16
Pb																
1	35.1	33.	20.	42.	50.	16.	32.	36.	45.	36.	35.	17.	38.	30.	30.9	10.15
2	61.	55.	70.	76.	59.	26.	51.	65.	96.	64.	54.	35.	72.	60.	59.7	19.97

[a]Results eliminated for calculation of *X* and *S*.

TABLE 4—*Waste Material, bituminous coal fly ash 1 (all results except pH in mg/L).*

	Analyses									
Laboratory	pH	Ca	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
				ASTM METHOD A						
1	10.74	288.	0.0004	0.0021	<0.5	<0.00002	0.151	0.000037	<0.0003	0.170[a]
3	...	1180.	<0.0001	0.00062	<1.0	0.0008	0.046	0.00005	0.020	0.10
4	4.8	272.5	<0.045	0.48	0.11	0.04	0.210	0.0020	0.09	1.25[a]
5	10.71	150.	<0.01	0.01	0.1	<0.01	<0.05	<0.002	<0.05	0.14[a]
6	10.02[b]	240.[b]	...	...	...	...	...	<0.002[b]	...	...
6A	...	222.	<0.001	0.1	0.08	...	0.008	<0.05	0.01	0.2[a]
7	10.85	309.	...	0.08	...	<0.003	0.15	<0.002	<0.05	...
9	...	313.	...	...	<0.02	0.031	0.114	0.010[a]	0.05	...
10	11.8[c]	345.[c]	<0.01	0.4	79.0[a]	<0.02	0.12	0.0015[c]	<0.2	<0.1
11	10.77	288.	<0.01	0.0394	<0.1	<0.00005	0.15	<0.0001	<0.05	0.2783[a]
12	10.6[c]	255.[c]	...	...	...	...	...	0.0005[c]	...	...
13	6.10[b]	224.[b]	<0.05	<0.01	<3.0	<0.01	<0.05	<0.001	<0.05	<1.0
14	10.60	583.	...	...	...	...	...	...	...	...
15	6.73	...	0.05	0.296	<0.5	<0.01	<0.05	0.0008	<0.1	0.055
16	10.4	194.	0.002	...	<0.3	0.015	0.05	<0.001	<0.05	...
17	4.38	272.	0.002	0.707[a]	0.236	0.0062	0.120	<0.0003	<0.001	0.162[a]
18	10.55	353.7	<0.05	0.1	<1.0	<0.05	0.166	<0.001	<0.1	0.3[a]
19	4.9	200.	<0.01	2.11[a]	<0.3	0.02	0.23	0.0001	0.03	0.16[a]
Proposed EPA										
maximum	12.	...	0.50	0.50	10.	0.10	0.50	0.02	0.50	0.10
Limit										
minimum	3.									

NOTE: Additional Metals Analysis: Lab 6, Lab 7, Lab 10, and 2nd Replicate, Lab 19.

[a] Exceeds proposed EPA limit.

[b] Average of three values.

[c] Average of two values.

not within the range of one standard deviation for 50% of the parameters reported. Of more interest is that only four of the labs were within one standard deviation 80% of the time. Before the waste samples were sent to the laboratories, they were assisted in correcting their analytical problems. The wastes samples were distributed in March 1979, and the leach testing completed in early April. Analysis of all the leachate samples was completed in September, the preliminary test results were then compiled and analyzed. Statistical results indicated very poor precision, over 100% coefficient of variation for all wastes. Even the results obtained for the "standard fly ash" were equally poor (Table 4).

Phase II was completed, and the final report issued in Jan. 1980. As the result of the very poor precision data obtained during Phase II, the program's coordination committee (ASTM/NBS/DOE) concluded that the procedures and analytical methods had not developed to the point to yield reliable results.

Three key elements of variability were identified in the Phase II study: liquid to solid ratio, extraction equipment, and extraction time. As section chairman of the extraction group, I attempted to address these three variables. Using the "standard fly ash," leach tests were conducted utilizing different liquid to solids ratios; these ratios were 1 to 4, 1 to 8, 1 to 16, 1 to 20, 1 to 32, 1 to 64, and 1 to 100. Triplicate extractions were done for each ratio. In addition, the following extraction times were used: 1, 4, 8, 12, 16, 18, 24, 48, 72, and 144 h. All liquid to solid ratios and times were tested using both the ASTM shaker and the NBS rotating mixer. An ICAP was used to determine the concentrations of 48 metals in each leachate. The results of this study indicated that the better precision could be obtained by using a liquid to solid ratio of 1 to 20 and the NBS mixer. The study also indicated the extraction time did not play an important part in the test after an extraction time of 12 h.

A round-robin test program was conducted to verify the results of this study. The round-robin test data showed that better precision could be obtained if the changes were made. In June 1980, Method A, without these changes, was approved as a full standard by ASTM. In Jan. 1981, these changes were proposed to the committee and Method B withdrawn. Since that time, efforts to incorporate the changes necessary to improve the precision of the method have been gradually working their way through the concensus standards procedure within ASTM Committee D-34. The revised method has been approved by the society and will appear in the next publication of the annual book of standards.

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The Results of an Interlaboratory Study of a Column Method for Leaching Solid Wastes

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ABSTRACT: A method for generating aqueous leachates from solid wastes in a column apparatus has been drafted by ASTM Subcommittee D34.02.02 on Column Extraction Methods. The method was subjected to a five-laboratory study using fly ash as a waste material. The within laboratory relative standard deviation for metals (based on the results from three laboratories with multiple columns) was found to be approximately 35%. The overall single test reproducibility in terms of relative standard deviation (based on the results from these same laboratories) was approximately 55%. This excludes interlaboratory analytical effects because all analyses were performed by a central laboratory.

KEY WORDS: leachate, column, lysimeter, fly ash, extraction

The quality of the leachate generated by landfilled waste is one of the key determinants that separates environmentally acceptable and unacceptable disposal practices. Consequently, much effort has been expended (1) documenting the quality of leachates found in the field and (2) attempting to artificially generate leachates of comparable quality to those generated from similar wastes in the landfill environment. Although it would be very useful to have a universally applicable laboratory test capable of faithfully reproducing the quality of leachate generated from specific wastes in the landfill environment, there is virtually unanimous agreement that such a test does not exist. Furthermore, it is reasonable to suspect that such a test cannot exist because of the many identified and unidentified factors that influence leachate qual-

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ity. The investigator desiring advanced knowledge of leachate quality is, therefore, left to select one or more of the methods used to generate leachates from solid wastes and speculate, to a greater or lesser degree, about the relationship between artificial and "natural" leachate qualities. As a result of the degree of uncertainty involved in this process, many investigators choose to generate leachates by several different methods to help address the limitations of the individual methods. Possibly the most common methods included in such studies are well-mixed batch extractions, sequential well-mixed batch extractions and continuous extraction of waste packed in a column.

ASTM Method for Shake Extraction of Solid Wastes with Water (D 3987) [*1*], the EPA [*2*], and the American Foundrymen's Society [*3*] have developed standardized well-mixed batch extraction procedures, but no standard column leaching procedure exists. While it is unlikely that any single method can satisfy all of the potential applications for a column leaching test, the members of ASTM Subcommittee D34.02.02 on Column Extraction Methods have recognized that a standard method would (1) facilitate the comparison of results from different laboratories where such comparisons are desirable, (2) provide a guide for investigators interested in assembling a test apparatus without the benefit of previous experience with column leaching, and (3) provide at least an initial indication of the interlaboratory and intralaboratory precision of one column leaching procedure. Consequently, ASTM Subcommittee D34.02.02 has drafted a column leaching procedure for solid wastes and subjected it to round-robin testing using fly ash as a waste material.

Column Extraction Methods

There are a number of reasons why one might choose continuous column extraction methods rather than well-mixed batch extraction methods for generating leachates. First, it is reasonable to hypothesize that a column extraction apparatus it better able to simulate conditions that exist within the landfill environment than are well-mixed batch extraction methods. In particular, column methods probably provide more accurate simulations of the contacting conditions and the redox conditions. Second, column methods offer the potential for the laboratory examination of a variety of factors that may be difficult or impossible to examine using well-mixed batch extractions. If, for instance, an investigator is interested in the long-term effects of anaerobic biological activity on leachate quality, a column apparatus would probably be more suitable than a well-mixed batch apparatus. Third, if it is necessary to have a highly detailed description of leachate quality as a function of the amount of liquid having contacted the waste, a column method will provide data with less effort than required to conduct a large number of sequential batch extractions.

Column extraction methods are not without disadvantages, however. First,

column procedures appear to be somewhat less precise than batch extractions [4,5]. The results of this study tend to bear this out. Second, column devices are probably more difficult to operate because of the need to maintain a constant, usually low flow rate of liquid. Third, certain wastes will be difficult to examine in column tests because of the size of the individual particles that comprise the waste. Such particles can be either too large, resulting in uneven column packing and flow distribution, or too small, resulting in excessive resistance to leachate flow. Fourth, wall effects or internal cracks can cause uneven flow distribution but be difficult to detect.

The methods that have been used to conduct column extraction tests are varied. A few of the methods that have been discussed in the literature are summarized in Table 1. The table demonstrates that the tests can, for most purposes, be divided into two types: namely, those developed for leaching small quantities of homogeneous waste (usually industrial) in short periods of time and those developed for leaching large quantities of nonhomogeneous waste (usually municipal solid wastes) for long periods of time. The method drafted by ASTM, also shown in the table, in some respects falls between these two classes. The draft method can be generally characterized as a test for wastes without large particles, conducted over intermediate to long periods of time at moderate to high liquid application rates.

Description of the Draft Method

The column method used in this round-robin study employs a column comprised of a 30.5 cm length of cast acrylic pipe 10.2 cm in diameter. The end plates, constructed of 2.54-cm thick acrylic, contain porous polyethylene plates to help ensure good flow distribution at the column inlet and outlet. Deionized water is passed up through the saturated waste at a rate of one theoretical pore volume per day. The driving force for leachate flow is provided by a pressurized nitrogen head space in the influent reservoir. A drawing of the apparatus is contained in Fig. 1.

Waste is packed into the column in five lifts. After each lift is compacted to the desired degree, the surface of the lift is scarified and the next life added. The packing procedure is continued for 2.54 to 5.08 cm (1 to 2 in.) above the top of the column by temporarily extending the top of the column using a second piece of acrylic pipe held against the top of the column. The waste is then cut off at the top of the test column. The waste is saturated according to ASTM Test Method for Permeability of Granular Soils (Constant Head) (D 2434) for saturating soils in constant head permeameters. Additional driving force is, however, required to saturate some low permeability wastes in a reasonable time.

During the saturation procedure and thereafter, the waste must be viewed periodically to determine whether shrinkage is causing cracks. Vertical cracks and spaces between the waste and column wall are especially harmful

TABLE 1—*A summary of some of the column extraction methods reported in the literature.*

Waste	Column Diameter, cm	Length to Diameter Ratio	Approximate Leachate Application Rate, cm/day	Approximate Liquid to Solids Ratio, mL/Day per 1 g of Solids	Duration of Study, Days	Upflow or Down-flow	Column Composition	Reference
Lignite ash	1.7	36	1300	13.7	1.2	up	?	6
Varied industrial wastes	2.5	18	420	20	1	up	glass	4
Varied industrial wastes	5	12	72	13.4	3	up	glass	5
Raw and stabilized industrial waste	10.2	15	0.15	0.005	814	down	steel	7
Fly ash	10.2	3	13	0.25	32	up	plastic	the study reported upon herein
Varied industrial wastes	38.7	0.79	1	0.32 to 1.44	28 to 79	down	glass	4
Pulp and paper mill wastes	40.6	7.5	5.8	?	329	down	plastic	8
Municipal solid wastes	56	1.6	?	?	120	down	steel	9
Pulp and paper mill wastes	91	3.3	0.72	0.01	812	down	steel	10
Municipal solid waste and varied industrial wastes	91	2.3	0.15	0.0036	>365	down	steel	11
Municipal solid wastes	180	2	1	0.017	>200	down	concrete	4

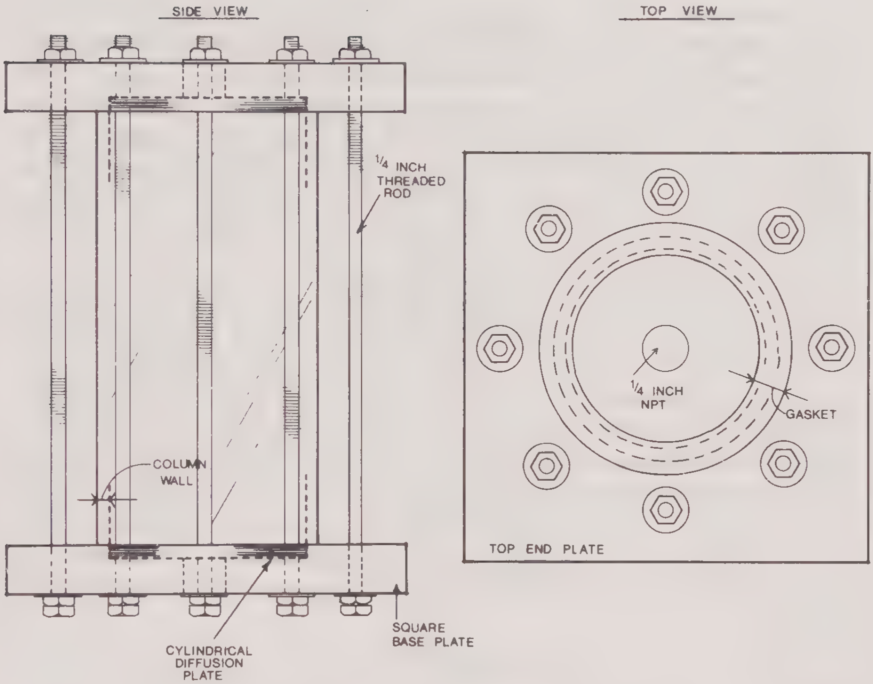

FIG. 1—*Column apparatus.*

and will usually dictate that the test be terminated. The column is to be shielded from the light at all other times.

Following saturation, the column test begins. Unless otherwise required, the flow of water into the column is maintained to displace one pore volume per day. Leachate is collected in a manner that minimizes contact with oxygen. Unless the objectives of the testing require otherwise, the first, second, fourth, sixteenth, thirty-second, and so forth, pore volumes are analyzed. It is useful to monitor specific conductance, pH, oxidation-reduction potential (ORP), and so forth, on a daily basis to facilitate interpretation of the results.

Description of Interlaboratory Study

The interlaboratory study reported upon herein was conducted using fly ash supplied by Conversion Systems Inc. Three of the laboratories ran triplicate columns while the remaining two laboratories ran single columns. All participants collected and preserved samples using a predetermined protocol and shipped them to a central laboratory for analysis. Several laboratories also monitored column effluent for indicator parameters.

The draft method calls for packing the waste in the column in a way that simulates the condition the waste will be in when it undergoes leaching in the field. To assure that all participants were simulating the same disposal scenario and to facilitate packing, participants were instructed to dry the fly ash at 100 to 110°C before packing the column, and to pack the columns with between 3680 and 4000 g of fly ash solids. The packing technique was not specified, however. The columns were saturated according to ASTM D 2434 unless additional driving force was necessary. The columns were operated at a leachate exchange rate of one pore volume per day.

Samples were collected in ways determined by the individual laboratories to minimize contact with air. The first, second, fourth, sixteenth, and thirty-second pore volumes were each collected, mixed, and poured into two well-washed polyethylene sample bottles. Nitric acid was added to one of the two bottles to preserve the sample for metals analysis. Samples were not filtered. SOHIO Inc. conducted all analyses for specific inorganic constituents at a single laboratory using inductively coupled plasma (ICP) analysis. SOHIO Inc. also analyzed the unpreserved samples by ion chromatography to determine the concentrations of specific anions. The results of the ion chromatography analyses were not available at the time this paper was being prepared, however.

Results

Although the amounts of dry fly ash packed into the columns at the five participating laboratories varied by more than the original target range (3680 to 4000 g), a far more significant difference was found in the pore volumes reported by the laboratories. Laboratory D calculated a pore volume of 70% greater than the other four laboratories. This was found to be caused by a computational error. The difference, however, resulted in Laboratory D passing almost twice as much water through the waste as used by the other laboratories. This would be expected to dilute the samples from Laboratory D relative to the other laboratories. Because of this, the data were evaluated with and without Laboratory D included. The estimated method precision was not affected by the inclusion of Laboratory D so all results reported herein include Laboratory D.

The results of monitoring leachate pH, conductivity, and total solids at Laboratory C are shown in Figs. 2 through 4. Laboratory precision for these parameters at Laboratory C appears to be acceptable. It should be noted that because of observations of precipitate formation in the leachate collection vessel, several measures were attempted at Laboratory C to minimize the contact of the sample with air. The most successful means found was the use of two water traps in series, both containing argon head spaces. This was implemented between the collection of the second and third pore volumes. Measurements of ORP provided evidence that this was successful in minimizing the amount of air contacting the leachate.

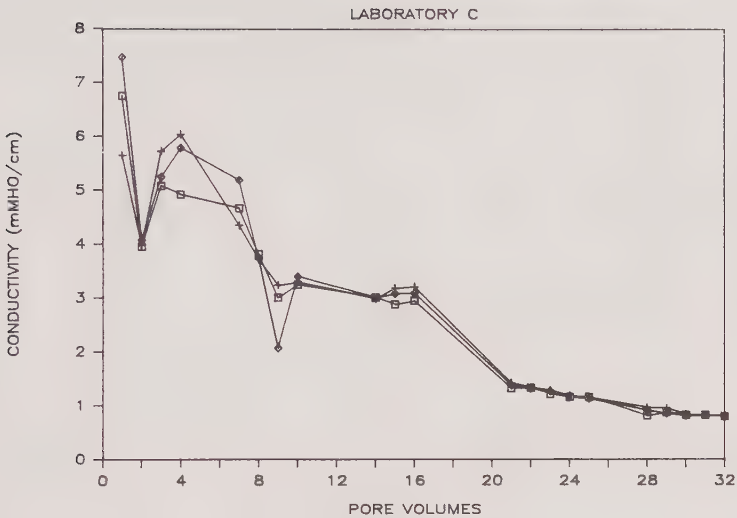

FIG. 2—*Leachate conductivity.*

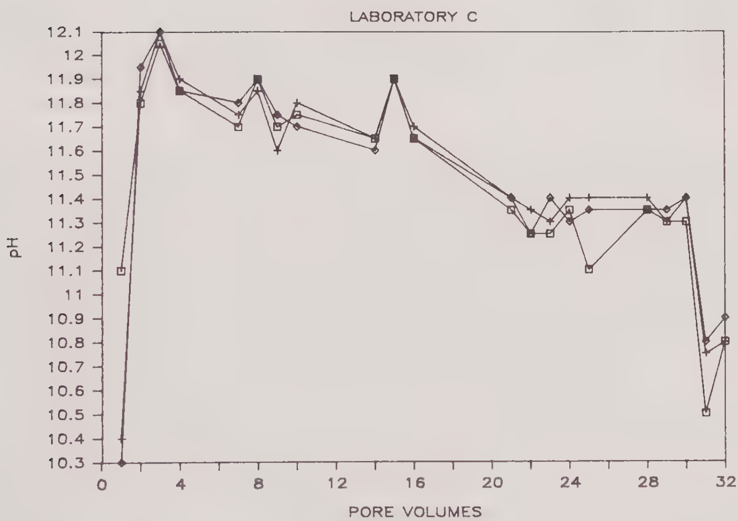

FIG. 3—*Leachate pH.*

The laboratories running triplicate columns found reasonable within laboratory precision with respect to leachate metal content. There was comparatively less agreement between the results from different laboratories. The data from all five laboratories were subjected to analysis of variance to identify instances where differences between laboratory results might be statistically

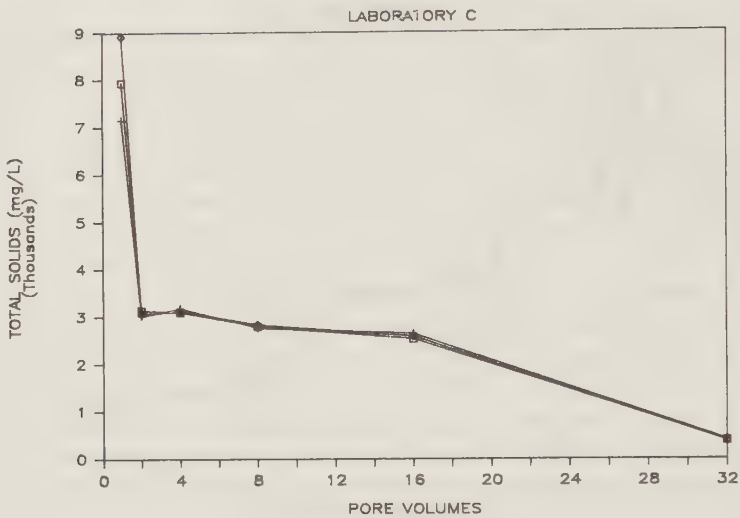

FIG. 4—*Leachate total solids.*

significant. The results, contained in Table 2 illustrate that there were frequent instances of significant differences between laboratory results at the 0.05 significance level. (Concentrations of arsenic, barium, bismuth, cadmium, manganese, lead, selenium, and titanium were found at concentrations above detection levels in only isolated instances.)

The data from Laboratories B, C, and D were analyzed further according to ASTM Practice for Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods (E 691) to identify the components of variance caused by within laboratory and between laboratory effects. Because all chemical analyses were conducted by a central laboratory, the within laboratory variance includes both single laboratory analytical variance and single laboratory leaching procedure variance. The fraction of the variance caused by differences between laboratories reflects only the precision of the leaching test (and associated procedures) and does not reflect interlaboratory chemical analysis effects. Table 3 contains the pooled within laboratory relative standard deviations and the overall method variability in terms of relative standard deviation. Although the major characteristic of the relative standard deviations is their inconsistency, it can be observed that overall the pooled within laboratory relative standard deviation was approximately 35% while the overall variability, expressed as a relative standard deviation, was approximately 55%.

Table 4 presents the data in terms of (1) the mean concentration for each element in each pore volume generated by the three laboratories with triplicate columns and (2) the overall relative standard deviations.

TABLE 2—*Results of analysis of variance,* F *statistic. (Numbers in parentheses are the number of values out of ten or eleven that were below the detection limit but treated as being at the detection limit.)*

Element	Pore Volume 1	2	4	8	16	32
Al	9.79 (0)[a]	13.3 (2)[a]	2.17 (1)	6.12 (0)[a]	74.1 (0)[a]	45.8 (0)[a]
Ca	7.86 (0)[a]	14.1 (0)[a]	37.76 (0)[a]	14.2 (0)[a]	51.6 (0)[a]	22.3 (0)[a]
Co	15.7 (3)[a]	...	...	...	...	...
Cr	33.4 (0)[a]	1.64 (0)	5.59 (0)[a]	5.05 (0)[a]	6.48 (2)[a]	...
Cu	4.19 (0)	1.67 (0)	6.27 (0)[a]	6.83 (0)	2.10 (5)	...
Fe	13.0 (0)[a]	1.28 (0)	1.81 (0)	2.25 (0)	2.86 (4)	...
K	23.0 (0)[a]	21.9 (2)[a]	4.54 (0)[a]	2.06 (1)	4.74 (3)[a]	...
Li	4.11 (0)	3.57 (0)	5.31 (4)[a]	...	...	...
Mg	3.16 (3)	...	...	...	...	...
Mo	21.8 (0)[a]	36.4 (0)[a]	1.77 (0)	647 (0)[a]	2.71 (3)	...
Na	27.5 (0)[a]	4.71 (0)[a]	3.70 (0)	7.27 (0)[a]	2.72 (1)	...
Ni	...	...	...	3.43 (3)	2.52 (0)	8.22 (1)[a]
P	...	...	1.42 (3)	1.34 (4)	0.55 (4)	...
Si	...	...	...	...	7.09 (1)[a]	5.18 (0)[a]
Sr	8.49 (0)[a]	2.23 (0)	4.36 (0)	135.0 (0)[a]	7.51 (5)[a]	...
V	1.71 (3)	19.0 (1)[a]	6.19 (1)[a]	6.44 (0)[a]	2.73 (2)	10.3 (1)[a]
Zn	0.78 (2)	...	...	...	...	...

NOTE: Those data sets containing more than five values (out of ten or eleven) below the detection limits, were not subjected to analysis of variance. These data sets are indicated by dashes above (-).

[a]Significant F at the 0.05 significance level.

Table 5 separates the total variance into within laboratory and between laboratory components. Again the results are highly variable, but overall it can be stated that within laboratory effects accounted for approximately 40% of the total variance while between laboratory effects accounted for approximately 60% of the variance. If each laboratory had performed its own chemical analyses, the fraction of the total variance caused by interlaboratory effects would have been greater. Indeed, it is noteworthy that while Webster et al. [*12*] found in a study of batch extraction procedures that interlaboratory analytical variance was a small component of the total (on the order of 5%), Rose et al. [*13*] generated data in a similar study suggesting that on the order of one-half of the overall variance observed was due to interlaboratory analytical effects. Clearly, the data in Tables 3, 4, and 5 must be used recognizing that interlaboratory analytical effects may significantly impact the overall interlaboratory precision.

In the course of undertaking this round-robin study, several considerations were identified that could be important to method precision. First, the importance of careful determination of column weight, waste specific gravity, and moisture content should be emphasized to help ensure accurate determination of pore volume. Second, any liquid collected during the saturation pro-

TABLE 3—*Method precision, percent relative standard deviations (pooled within-laboratory relative standard deviation/overall interlaboratory variability of a single test result in terms of relative standard deviation).*

Element	Pore Volume						
	1	2	4	8	16	32	Average[a]
Al	61/130	22/62[b]	44/54	30/40	29/85	10/50	35/72
Ca	9/20	5/16	6/28	7/14	14/75	13/42	9/33
Co	25/64[b]	...	...	...	...	...	...
Cr	13/51	12/15	16/33	8/8	17/33[b]	...	12/27
Cu	25/33	8/10	12/22	18/26	33/43[b]	...	16/23
Fe	88/140	16/18	20/26	16/18	27/40[b]	...	35/51
K	24/82	28/110	63/120	93/100[b]	48/80[b]	...	38/104
Li	34/50	75/130	63/120	...	...	...	57/100
Mg	130/170[b]	...	...	...	...	...	...
Mo	5/10	13/60	59/79	17/69	51/77[b]	...	24/55
Na	24/87	56/100	50/86	28/39	46/59	...	41/74
Ni	...	...	...	50/86[b]	36/41	21/34	61/38
P	...	...	64/71	85/85[b]	67/73[b]	...	64/71
Si	...	...	...	...	34/48	22/29	28/39
Sr	19/42	16/18	28/52	4/22	36/75[b]	...	17/34
V	49/53[b]	10/27	30/60	16/18	24/33[b]	14/24	18/32
Zn	99/100[b]	...	...	...	...	...	...
						Average	33/54

NOTE: Because all chemical analyses were performed by a single laboratory, the total variance does not contain an interlaboratory analytical component.

[a]Average values are based only on data without asterisks.

[b]Based on data sets that contain 1 to 3 values below detection limits (out of 9 values). Those values below detection limits are assigned the detection limit in the calculations. If more than 3 values are below the detection limit, the data were not analyzed.

cess should be considered to be part of the first pore volume. Third, leachate should be collected in a flask containing an inert gas headspace and protected from the atmosphere by a water trap attached to the outlet of the collection flask.

Discussion

One primary objective of this round-robin study was to determine whether the draft method was precise enough to offer hope that a final method with acceptable precision could be developed. The reader's initial reaction to the data previously presented is probably that the method is very imprecise. It is useful, however, to compare the results of this study with other studies of column and batch extraction methods. In making these comparisons, it is necessary to greatly condense the results of such studies. This condensation process may in some instances tend to obscure the true meaning of the data so the reader is encouraged to review the studies first hand.

TABLE 4—*Mean concentrations (mg/L) and total interlaboratory percent relative standard deviations (mean/percent RSD).*

Element	Pore Volume					
	1	2	4	8	16	32
Al	13/130	0.75/62[a]	0.55/55	0.45/40	1.1/85	3.6/50
Ca	720/20	880/16	890/28	730/14	460/75	130/42
Co	0.20/64[a]	...	...	...	...	...
Cr	0.50/51	0.25/15	0.25/33	0.20/8	0.20/33[a]	...
Cu	0.50/33	0.45/10	0.45/22	0.30/26	0.20/43[a]	...
Fe	2.2/140	0.25/18	0.25/26	0.25/18	0.15/40[a]	...
K	590/82	55/110	30/120	3.0/100[a]	6.1/80[a]	...
Li	21/50	4.3/130	0.70/120	...	...	...
Mg	10/170[a]	...	...	...	...	...
Mo	46/10	33/60	5.8/79	1.0/69	0.40/77[a]	...
Na	370/87	19/100	5.4/86	1.7/39	2.0/59	...
Ni	...	...	...	0.30/86[a]	0.40/41	0.50/34
Pi	...	...	0.50/71	0.30/85[a]	0.25/73[a]	...
Si	...	...	...	...	3.7/48	7.1/29
Sr	4.8/42	6.5/18	2.8/52	0.80/22	0.45/75[a]	...
V	0.30/53[a]	0.25/27	0.30/60	0.20/18	0.20/33[a]	0.25/24
Zn	1.4/100[a]	...	...	...	...	...

NOTE: Only data from the three laboratories running three columns each are used here. Also the total relative standard deviation does not include interlaboratory analytical effects.

[a]Based on data sets that contain one to three values below detection limits (out of nine values). Those values below detection limits are assigned the detection limit in the calculations. If more than three values are below the detection limit, the data were not analyzed.

Rose et al. studied the precision of the EPA acid extraction procedure on utility wastes [*13*]. Because the data were treated as being lognormally distributed, the results are stated in terms of 90% confidence multipliers instead of relative standard deviations. (If the geometric mean is multiplied and divided by the 90% confidence multiplier, the results are the upper and lower limits of the interval into which one can be 90% confident that any single value will fall.) If one excludes those data characterized as being "less reliable" because of detection limit effects, the overall 90% confidence multiplier for metals data averaged approximately 1.9 for the data reported in the publication by Rose et al. In other words, one can be 90% confident that, overall, any single analysis would lie between approximately 50% of the geometric mean and 200% of the geometric mean. In total, the data in the Rose et al. study suggest that on the order of half of the total variance was due to interlaboratory analytical effects. Intralaboratory analytical effects may have accounted for 20% of the variance while interlaboratory and intralaboratory extraction procedure effects may each have accounted for approximately 10% of the total. The remaining 10% was unaccounted for.

The precision data reported by Rose et al. are highly variable, and generalizations tend to obscure their character. It is useful to note, however, that if

TABLE 5—*Components of variance. Percent of total variance caused by variance (within laboratories/between laboratories).*

Element	Pore Volume 1	2	4	8	16	32	Average[a]
Al	21/79	13/87[b]	65/35	56/44	12/88	4/96	32/68
Ca	18/82	10/90	5/95	22/78	4/96	10/90	12/88
Co	15/85[b]	. . .	. . .	. . .	. . .	. . .	. . .
Cr	6/94	68/32	24/76	100/0	26/74[b]	. . .	50/50
Cu	56/44	57/43	29/71	50/50	58/42[b]	. . .	48/52
Fe	38/62	83/17	62/38	82/18	46/54[b]	. . .	66/34
K	9/91	7/93	29/71	81/19[b]	36/64[b]	. . .	15/85
Li	46/54	36/64	26/74	. . .	. . .	. . .	36/64
Mg	62/38[b]	. . .	. . .	. . .	. . .	. . .	. . .
Mo	26/74	5/95	55/45	6/94	44/56[b]	. . .	23/77
Na	8/92	28/72	34/66	51/49	60/40	. . .	36/64
Ni	. . .	. . .	. . .	34/66[b]	74/26	38/62	56/44
P	. . .	. . .	81/19	100/0[b]	84/16[b]	. . .	81/19
Si	. . .	. . .	. . .	. . .	50/50	58/42	54/46
Sr	22/78	82/18	28/72	3/97	23/77[b]	. . .	34/66
V	85/15[b]	14/86	25/75	84/16	56/44[b]	33/67	39/61
Zn	98/2[b]	. . .	. . .	. . .	. . .	. . .	. . .
							42/58

NOTE: Because all chemical analyses were performed by a single laboratory, the total variance does not contain an interlaboratory analytical component.

[a]Average values are based only on data without asterisks.

[b]Based on data sets that contain from one to three values below detection limits (out of nine values). Those values below detection limits are assigned the detection limit in the calculations. If more than three values are below the detection limits, the data were not analyzed.

the interlaboratory variance is removed from the total, the overall 90% confidence multiplier is reduced to approximately 1.35. This can be compared to the study reported upon herein where the overall relative standard deviation for a single observation was about 55%. This translates into a 90% confidence interval bracketed by approximately plus and minus 90% of the mean. This interval appears to be larger than the comparable interval calculated for the batch extraction procedure from the data of Rose et al.

Webster et al. have studied the precision of the ASTM and EPA extraction procedures [*12*]. The overall relative standard deviation for six metals, including interlaboratory analytical variance, averaged approximately 80 to 90% for both batch extraction methods. Seventy percent of the total variance was related to between laboratory effects while 30% was due to within laboratory effects. In general, analytical variance was found to be small, usually 5% or less of the total. The extraction methods used by Webster et al. appear to be somewhat less precise than the column method discussed herein.

Ham et al. [*14*] examined three well-mixed batch extraction procedures and provided precision data based on triplicate extractions of paint waste per-

formed at a single laboratory. The relative standard deviations for metals data were generally less than 15%, which is lower than the 35% within laboratory relative standard deviation found with the column procedure discussed herein.

McKown et al. [*15*] examined a variety of well-mixed batch extraction procedures applied to multiple wastes in a single laboratory. The tables containing the precision results for (POTW) sludge reveal that the overall single laboratory relative standard deviations for metals data averaged 23 and 38% for the NBS and ASMCO extractors, respectively, when the EPA acid extraction medium was used. When other extraction media were used in the NBS extractor, the overall within laboratory relative standard deviations were normally below 30%. This is lower than the corresponding relative standard deviation determined in this study.

Limited duplicate test results from a single laboratory using the EPA extraction procedure are contained in Ref *16*. The average relative standard deviation for metals data can be calculated to be approximately 35%, comparable to that documented herein.

Brown et al. [*16*] have reported the results of a single laboratory study of four well-mixed extraction procedures applied to energy production wastes. The average relative standard deviations of the metals data for the EPA, ASTM A, ASTM B, and carbonic acid extractions can be calculated to be 9, 12, 28, and 9%, respectively. All of these are below the within laboratory relative standard deviation reported herein.

There are also data available on the intralaboratory precision of column extraction techniques. Francis et al. [*4*] leached industrial wastes with artificial municipal solid waste leachate in field columns 180 cm in diameter. The relative standard deviation for metals concentrations based on four replicate columns was approximately 50%. This is greater than documented herein.

Reference *11* contains data from triplicate 91-cm-diameter municipal solid waste lysimeters. The average relative standard deviation for cadmium, chromium, and lead concentrations was approximately 60%. This again is higher than reported herein. (It is based on a fewer number of metals, however.)

There are several sources of information comparing continuous column extractions with sequential well-mixed batch extractions. Jackson et al. [*5*] compared in a single laboratory, multiple batch extractions of four industrial wastes with extractions accomplished in Columns 5 cm diameter. The sequential batch procedure proved to be more reproducible and more aggressive. The average relative standard deviations for metals data were 42% for the column extraction and 11% for the sequential batch extraction. The column extraction figure is slightly higher than the corresponding figure found in this round-robin study while the batch extraction figure is well below this study's figure.

Francis et al. [*4*] have also compared sequential batch extraction with extraction accomplished in a 2.5-cm-diameter column using four different ex-

traction media. Although precision data are not provided, visual examination of 100 data plots containing batch and column data reveals approximately 10 instances where the column data appear more reproducible, 40 where the sequential batch extraction data appear more reproducible, and 50 where the difference, if any, is not obvious.

Although the preceeding information is limited and sometimes inconsistent, several generalizations can be made.

1. The column procedure used herein appears to be somewhat less reproducible than many well-mixed batch extraction procedures.
2. Sequential batch extraction procedures may be more reproducible than column procedures in general.
3. The precision of this column method is not unusually low compared to several other column methods that have been reported in the literature.

Conclusions

1. The within laboratory relative standard deviations for metal concentrations in those leachates generated by three laboratories with triplicate columns averaged approximately 35%.
2. The total methods (single test) reproducibility in terms of relative standard deviation was approximately 55%. This does not include any interlaboratory analytical effects since all chemical analyses were performed by a single laboratory.
3. This column method as applied in this study appears to be less precise than many well-mixed batch and well-mixed sequential batch extraction methods. The precision is good, however, compared to the published results of several other column studies.
4. It is impossible for this, or any extraction method, to universally duplicate field conditions. Consequently, when this, or any extraction method is applied with the intention of simulating field conditions, the results must be used with caution.

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Batch Type 24-h Distribution Ratio for Contaminant Adsorption by Soil Materials

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ABSTRACT: An investigation was undertaken to develop a standardized batch adsorption procedure that uses the initial and 24-h solution concentrations to calculate a distribution ratio R_d between solutes and soil materials. In developing these procedures, it was found that the method of mixing the solute-soil mixtures influenced the amounts of solute adsorbed. To ensure reproducibility, a National Bureau of Standards rotating tumbler was adopted as the mixing system. An interval of 24 h was established as a valid operational definition of reaction time for determining R_d values.

Interlaboratory testing was conducted with arsenic and cadmium using soil materials having a range in physiochemical properties. The interlaboratory coefficients of variation (CV) were generally less than 10%. The precision of an R_d measurement for a species that meets the criteria of being stable and nonvolatile should yield percent CV within the range established. The method has not been tested for organic solutes and is not considered viable for volatile chemical species. The method is considered a reliable and useful technique for comparing the adsorption properties of various soil materials under a given set of conditions.

KEY WORDS: attenuation, soil materials, adsorption, batch test, adsorption procedure, K_d value, K_p value, National Bureau of Standards (NBS) rotating tumbler mixing method, adsorption kinetics, interlaboratory adsorption testing, soil chemical screening, contaminant mobility test

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The "batch-test" adsorption procedure has been widely used since the 1950s. The overall objective of batch adsorption procedures has been to characterize the capacities of unconsolidated geological materials, such as clay minerals and soils, to adsorb a given chemical species from solution. One application of this type of data is to predict the attenuation of pollutants and the potential impact of leachate contaminants from wastes on ground-water quality in the vicinity of land disposal facilities and hence, in site selection and evaluation of various clay materials for their potential use as landfill liners.

The evaluation of the adsorption properties of the earth materials has been generally approached by laboratory studies where experimental variables can be controlled and continuously monitored. In principle, the batch adsorption technique is relatively simple and accounts, in part, for its popularity. The technique consists of determining a partitioning or distribution ratio R_d between chemical species and the soil material by mixing a solution of known composition and concentration with a given mass of adsorbent (soil material) for a period of time. The solution is then separated from the adsorbent and chemically analyzed to determine changes in solute concentration. However, apart from the inherent variability of different soils, there are a number of experimental parameters that may affect the results of the test. For inorganic solutes, these parameters include time, temperature, method of mixing, the soil-to-solution ratio, moisture content, and the composition and concentration of the solution. The ability of the scientific engineering community to obtain batch adsorption data of known precision and accuracy under standardized test conditions has been hampered because no standard method has been available. It is the desire of ASTM Subcommittee D34.02.03 on Predictive Methods and Field Verification to partially fill this void by developing a standard method for obtaining batch-type adsorption data.

Approach

The approach to developing this batch adsorption procedure has been based on the premise that it should be reliable, rapid, and as simple and flexible as possible. The procedure is meant to allow for a rapid (24-h) index of the soil material's ability to adsorb given chemicals or leachate constituents from solution. The method was developed to be useful for screening or determining a comparative ranking among a large number of samples. The 24-h time is used to make the test rapid, convenient, and to minimize microbial degradation or other such interferences that may be a problem with procedures that require longer times to obtain results. Because of this time constraint, the determined distribution ratio R_d may not be an equilibrium or steady state constant (K_d or K_p), but rather an estimate of the ability of the soil material to adsorb or attenuate a given chemical species from a given solution or leachate over a 24-h period. However, many reactions do reach equilibrium or

steady state conditions within 24 h, and if steady state conditions can be demonstrated for a given soil material and solution, then considering the distribution ratio R_d as a steady state or equilibrium constant K_d may be appropriate.

The appropriateness and reliability of the procedure was addressed through an extensive peer review process and an interlaboratory testing program. A series of three round-robin tests with up to seven participating laboratories was carried out under the auspices of ASTM subcommittee D34.02.03. A central laboratory was assigned to provide the necessary documentation, soils, and chemicals to carry out the procedures. This laboratory was also responsible for the analysis of the post-procedure solution. The above mentioned logistics were necessary to reduce the possibility of errors and reduce variability not inherent to the procedure (that is, specimen preparation, analysis methods, and equipment).

Further development of the procedure was based on the premise that it would be most useful if it were flexible enough to reasonably accommodate potential users and have a well founded scientific rationale. A flexible procedure would allow the investigator to use various techniques and equipment within the procedure without significantly altering the results.

Methods and Materials

The proposed ASTM 24-h batch adsorption procedure is presented in the Appendix appended to this paper.

Seven soil materials were collected and characterized (Table 1): the surface horizon of Catlin silt loam and Cecil clay loam, the subsoil of a Sangamon soil (paleosol), a kaolinite clay, and three lithofacies of the Vandalia Till (the surficial glacial till in south-central Illinois). These samples were chosen to represent a range of characteristics potentially significant in waste disposal; they vary considerably in texture, mineralogy, surface area, pH, cation exchange capacity, and organic carbon content.

All solutions were analyzed by inductively coupled argon plasma emission spectroscopy (ICAP). The methods and performance characteristics for the instrument are given by Krapac et al. [*1*].

Results and Discussion

Equilibration Time

The appropriateness of the 24-h time interval for the proposed R_d procedure was investigated. Some investigators have used equilibration times on the order of days. However, adsorption per se is generally regarded as a rela-

TABLE 1—*Selected physical and chemical properties of soils and soil materials used in the development of the ASTM 24-h batch-type distribution ratio* (R_d) *procedure.*

Soil	pH(1:1)[a]	Sand, %	Silt, %	Clay, %	Organic Carbon, %	N_2 Surface Area,[b] m^2/g	CEC[c], meq/100 g	Clay Analyses, %			Other Clay-Sized Minerals
								Illite	Kaolinite	Expandables	
Catlin silt loam (*A*1 horizon of a Typic Arguidoll)	6.1	11	69	21	4.04	14.8	18.1	55 to 67	5 to 15	24 to 30	...
Cecil clay loam (*Ap* horizon of a Typic Hapludult)	4.6	32	17	51	ND[d]	29.7	3.79	5 to 6	79 to 92	2 to 16	goethite, hematite
Kaolinite clay (Pike Co., IL)	8.1	0	0	100	0.51	34.2	15.1	8	87	5	quartz
Sangamon paleosol (*Btb* horizon of a buried soil in glacial till)	6.1	45	25	30	0.10	22.9	16.73	33 to 36	7 to 14	50 to 60	...
Vandalia till member (Illinoian till)											
altered	7.4	45	38	17	0.18	7.3	6.60	71 to 77	3 to 10	18 to 19	...
unaltered	7.5	45	40	15	0.34	5.6	4.94	75 to 82	4 to 19	6 to 9	...
ablation phase	6.4	56	21	23	0.10	10.6	10.45	32 to 58	2 to 6	32 to 39	goethite

[a]pH of 1:1 soil:water soil paste.
[b]Surface area measured by N_2 adsorption by BET method.
[c]Cation exchange capacity.
[d]No determination available.

tively fast reaction, and subsequent removal of a solute from solution may be attributed to other processes. The ambiguity of equilibration times has been acknowledged as a major problem in adsorption studies [2]. The U.S. Environmental Protection Agency (EPA) [3] suggested that the equilibrium time should be defined as the minimum amount of time needed to establish a rate of change of the solution concentration equal to or less than 5% per 24-h interval. The efficacy of this operational definition for equilibrium was evaluated using several soil materials and solutes. Each of the adsorbents was exposed to solutions containing various solutes for periods of time up to 72 h (Fig. 1). All of the cationic soil-solute systems in this study were found to be in equilibrium within 24 h as defined by this operational definition. In contrast, the anions phosphate and arsenate had not reached steady state concentrations within 24 h in some cases. However, they only changed by an additional 10% during the next two 24-h intervals. The concentrations of most solutes are expected to achieve steady state within 24 h, and the worst cases observed in this study were close to steady state concentrations within 24 h. These results were considered justification for use of the 24-h reaction time as a practical constraint to allow the test to be rapid and yet produce reliable relative data.

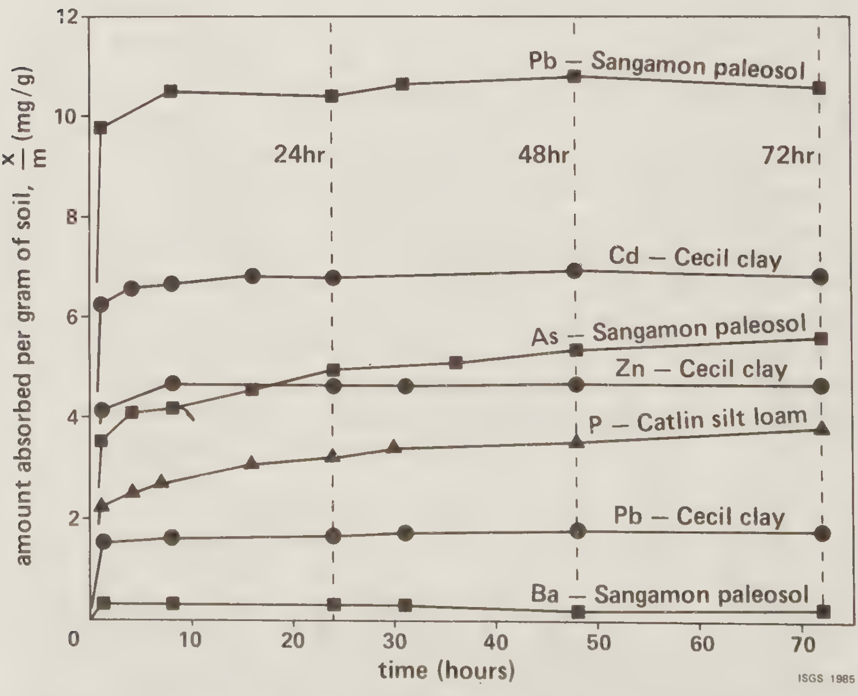

FIG. 1—*Equilibration time determinations for several representative soil-solute combinations.*

Mixing Method

A first generation procedure was formulated around the ASTM-A, water shake extraction procedure [*4*]. A sensitivity analysis of this early procedure made by a number of participating laboratories found that the method of mixing influenced the amount of cadmium and arsenic adsorbed by Catlin silt loam soil; when shaking was more vigorous, greater amounts of solute were adsorbed. The results from the first sensitivity analysis are reported in Table 2. It should be noted that arsenic and cadmium solutions were made from KH_2ASO_4 and $CdCO_3$ salts in all experiments used to develop this procedure. Large differences in concentrations between the laboratories yielded interlaboratory coefficients of variation (%CV) in excess of 145%. This first round-robin interlaboratory study was a clear example of why a standard test method was needed.

To improve the consistency of interlaboratory results, a National Bureau of Standards (NBS) rotating tumbler was tested as the mixing system. A second sensitivity analysis was carried out (Tables 3 and 4). The coefficient of varia-

TABLE 2—*Results of sensitivity analysis for cadmium and arsenic adsorption by Catlin silt loan where shakers and a paddle stirrer were used as the mixing method.*

		High[a], μg/mL[b]		Low[c], μg/mL[b]		Shaker Rate	
Lab	Sample	Cd	As	Cd	As	Strokes/min	Throw, cm (in.)
	1	16.87	...	0.080	...		
A	2	13.24	...	0.034	...	59	7.62 (3)
	3	11.36	...	0.022	...		
	1	83.8	186	0.166	7.92		
B	2	88.2	186	0.159	7.77	70	3.81 (1.5)
	3	86.7	185	0.176	7.91		
	1	1.88	128	<0.01	0.43		
C[1]	2	1.77	131	<0.01	0.38	100	3.18 (1.25)
	3	1.70	127	<0.01	0.46		
	1	26.5	162	0.064	5.00		
C[2]	2	21.5	168	0.057	4.78	70	3.18 (1.25)
	3	10.0	175	0.096	5.81		
	1	3.2	...	<0.01	...		
D	2	3.2	...	<0.01	...	paddle stirrer used	
	3	2.9	...	<0.01	...		
	1	2.7	130	0.007	0.53		
E	2	2.9	134	0.008	0.55	not known	
	3	2.7	130	0.008	0.55		
Overall mean		21.2	153.5	0.073[d]	3.51		
S		30.8	25.6	0.064	3.32		
CV (%)		145.4	16.7	87.7	94.5		

[a]Initial solution concentration of 200 mg/L.
[b]Represents post-procedure solute concentrations.
[c]Initial solution concentration of 10 mg/L.
[d]Does not include values less than the detection limit.

TABLE 3—*Cadmium adsorption data from Catlin silt loam using an NBS rotating tumbler as the mixing method.*

Lab	Initial Concentration, μg/mL	24-h Concentration, μg/mL	R_d, mL/g	Initial Concentration, μg/mL	24-h Concentration, μg/mL	R_d, mL/g
			A. Rep			
1	200	35.7	92.0	10.1	0.114	1734
2	200	36.2	90.5	10.1	0.126	1567
3	200	34.6	95.6	10.1	0.125	1580
			B.			
1	200	31.8	105.8	10.0	0.110	1798
2	200	35.8	91.7	10.0	0.135	1461
3	200	36.8	88.7	10.0	0.165	1214
			C.			
1	200	35.6	92.4	10.0	0.127	1554
2	200	35.6	92.4	10.0	0.127	1554
3	200	35.0	94.3	10.0	0.132	1495
			D.			
1	190	31.0	102.5	9.8	0.130	1487
2	190	30.0	106.6	9.8	0.110	1761
3	190	31.0	102.5	9.8	0.120	1613
	$\bar{X}$	34.1	96.3	$\bar{X}$	0.127	1568
	S	±2.4	±6.3	S	±0.01	156
	CV (%)	7.1	6.6	CV (%)	7.94	9.97

tion (% CV) between the mean values for each laboratory reflects, in part, the precision of the mixing method. The coefficient of variation of R_d values based on initial cadmium and arsenic concentrations of 10 mg/L and 200 mg/L were less than 10 and 31% for cadmium and arsenic, respectively. These results can be compared with those from the first round using shakers, which were as great as 145% for similar concentrations (Table 2). Because all other parts of the procedure were the same in both cases, the mixing method was concluded to be a primary contributor to the variation between the interlaboratory means. The NBS tumbler was adopted as the method of choice because of the much lower coefficient of variation between laboratory means.

Effects of Temperature and Filtration/Centrifugation

Major points in the methodology requiring special equipment were investigated by intralaboratory testing to determine the degree of flexibility that could be accommodated, without significantly affecting the results of the test. The effects of temperature and two methods of solid phase separation, filtration and centrifugation, were evaluated (Table 5). These results and those from several other tests with other chemical species and soil materials indi-

TABLE 4—*Arsenic adsorption data from Catlin silt loam using an NBS rotating tumbler as the mixing method.*

Lab	Initial Concentration, µg/mL	24-h Concentration, µg/mL	R_d mL/g	Initial Concentration, µg/mL	24-h Concentration, µg/mL	R_d, mL/g
			A. Rep			
1	205	180.3	2.74	10.0	5.76	14.72
2	205	180.3	2.74	10.0	5.85	14.18
3	205	182.0	2.53	10.0	5.89	13.95
			B.			
1	200	175.5	2.79	10.0	5.52	16.23
2	200	178.0	2.47	10.0	5.40	17.03
3	200	170.7	3.43	10.0	5.48	16.49
			C.			
1	200	186.3	1.47	10.0	5.57	15.90
2	200	177.3	2.56	10.0	5.64	15.29
3	200	175.0	2.85	10.0	5.59	15.77
			D.			
1	200	160.0	5.0	12.0	6.80	15.29
2	200	180.0	2.22	12.0	6.80	15.29
3	200	180.0	2.22	12.0	6.90	14.78
	$\bar{X}$	177.1	2.75	$\bar{X}$	5.93	15.42
	S	6.65	0.85	S	0.56	±0.92
	CV (%)	3.76	30.9	CV (%)	9.47	5.99

TABLE 5—*Temperature variation and effect of filtration versus centrifugation on arsenic adsorption by Catlin silt loam (200 µg/mL initial concentration).*

	mg As/kg in Solution					
	22°C		25°C		35°C	
Sample	Filter[a]	Centrifuge[b]	Filter	Centrifuge	Filter	Centrifuge
1	126.5	124.5	128.5	129.0	115.0	114.0
2	128.0	126.5	129.0	129.0	114.0	114.5
3	131.0	126.0	130.0	128.0	113.0	113.0
$\bar{X}$	128.5	125.7	129.2	128.7	114.0	113.8
S	2.29	1.04	0.764	0.577	1.00	0.764

[a]Filtration through 0.45 µm pore size membrane filter with vacuum.
[b]A 50-mL aliquot of the suspension was centrifuged at 1.6×10^4 rpm for 30 min.

cated that large temperature variations (greater than about 10°C) had a considerable effect on the amounts adsorbed, but small temperature changes of a few degrees had little effect on the overall results. Thus, strict temperature control was not deemed necessary and satisfactory results could be obtained, especially on a relative basis, for reactions carried out at room temperature

(22 ± 5°C). This specification was considered to greatly reduce the potential costs of equipment and space, increase the flexibility, and hence usefulness of the test for a small reduction in precision.

Filtration and centrifugation were investigated as methods of phase separation (Table 5). Overall, there were no significant differences between filtration and centrifugation with respect to solute concentrations. It was concluded that laboratories could be given the option in the procedure of either filtration or centrifugation without impairing the general usefulness of the results. However, the procedure (Appendix) notes that the affinity of the filtration membrane for the solute must be evaluated and that failure to do so may lead to erroneous results.

Soil: Solution Ratio

The soil: solution ratio of the proposed 24-h R_d procedure is 1:20. However, a single soil: solution ratio may not be satisfactory for all soils. The initial concentration of a weakly sorbing solute may not change enough to be measurable, and a solute with a strong affinity for the adsorbent may be adsorbed to an extent that the solution concentration is below analytical detection limits. The data given in Table 6 are for cadmium adsorption by two soil materials at soil: solution ratios varying from 1:4 to 1:1000 and serve to illustrate the range of concentration changes observed. Unfortunately, with inorganic compounds, a suitable soil: solution ratio cannot be determined a

TABLE 6—*Soil: solution ratio determination for the Sangamon paleosol and Vandalia ablation till using cadmium as the adsorbate.*

	Sangamon Cd Adsorbed		Vandalia Ablation Cd Adsorbed	
Soil: Solution Ratio	μg/g	%	μg/g	%
	Initial Concentration = 200 mg/L			
1:4	722	95.2	635	94.1
1:10	1631	86.1	1359	76.2
1:20	2792	73.7	2143	44.3
1:40	4246	56.0	3012	25.4
1:60	5165	45.4	3441	19.1
1:100	6250	33.0	3880	13.0
1:200	7500	19.8	4560	8.0
1:500	9250	9.8	4900	4.6
	Initial Concentration = 10 mg/L			
1:100	957	91.1	840	80.0
1:200	1736	82.7	1474	70.2
1:500	3178	60.5	2215	42.2
1:1000	4325	41.2	...	...

priori. The choice of the 1:20 ratio represents a compromise to accommodate an average range of expected concentration changes. If the results obtained using the "standard" 1:20 ratio are not useful for ranking particular soil material-solute combinations or reaching a technical conclusion, then additional testing at other ratios is needed.

Round-Robin Testing

The third round interlaboratory test was conducted using a soil:solution ratio of 1:20 and 70 g of soil. Results are given for cadmium and arsenic R_d values on three soil materials in Tables 7 and 8; interlaboratory CV varied between 8.2 and 10.3% for cadmium and 6.2 to 7.9% for arsenic.

Laboratory E (Tables 7 and 8) did not use a 70-g soil mass, but chose to use 17.5 g, while still maintaining the 1:20 ratio. The results from Laboratory E were of interest to the evaluation of the procedure since the differences between the results using 17.5 and 70 g were statistically insignificant. This implied that the procedure could be made more flexible because the mass of geomedia sample could be varied as long as the solid:solution ratio was maintained constant. To document this possibility, further tests were carried out with three soils (Table 9). The test procedures for this intralaboratory investigation were exactly the same as previous testing except that the mass of soil used was either 5 or 10 g; with the volume of solution and mixing bottle size reduced proportionately, that is, for a 10-g sample mass, the volume was 200 mL, and the bottle had a 250-mL capacity. The results of these tests (Table 9) indicated that the mass of soil could be varied if the soil:solution ratio was not changed.

Data Analysis

The data collected from the testing program were statistically analyzed, for the means $\bar{X}$, standard deviations s, and the percent coefficient of variation (% CV) of the post-procedure solution concentrations and corresponding R_d values (Tables 3, 4, 7, 8, and 9). Laboratory outliers and individual outliers, were identified and subsequently discarded based upon the criteria set forth by ASTM Committee D-19 on Water in ASTM Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water, (D 2777). Using these criteria, five data points were discarded from Laboratory A in Table 7. These data were eliminated because of gross sodium (Na) contamination of the post-procedure solution of greater than 500 μg/mL (approximately twice that of the other laboratory samples). Also, these data were shown to be statistically invalid via the test for individual outliers (ASTM D 2777). Laboratory E data could not be discarded according to the above criteria.

Since the change in mass size did not affect the statistical validity of Laboratory E data, the analysis of the intralaboratory testing was handled in a

TABLE 7—*Cadmium adsorption data for Sangamon paleosol, kaolinite clay, and the unaltered Vandalia till.*

Lab	Rep	Initial Concentration, μg/mL	Sangamon: 24-h Concentration, μg/mL	Sangamon: R_d, mL/g	Kaolinite: 24-h Concentration, μg/mL	Kaolinite: R_d, mL/g	Vandalia: 24-h Concentration, μg/mL	Vandalia: R_d, mL/g
A	1	97.6	21.3	71.6	24.2	60.6	79.6[a]	4.52
	2	97.6	58.0[a]	13.6	25.2	57.4	65.2[a]	9.94
	3	97.6	39.7[a]	29.2	23.6	62.7	48.8[a]	20.0
B	1	101.3	20.8	77.4	20.8	77.4	40.0	30.6
	2	101.3	20.5	78.8	20.6	78.3	39.2	31.6
	3	101.3	20.4	79.3	21.1	76.0	40.3	30.2
C	1	99.8	22.3	69.5	20.8	75.9	42.1	27.4
	2	99.8	22.5	67.8	21.3	73.7	42.2	27.3
	3	99.8	22.5	67.8	21.3	73.3	42.3	27.2
D	1	99.0	26.2	55.6	25.3	58.2	40.3	29.1
	2	99.0	24.6	60.4	22.3	68.7	44.6	24.3
	3	99.0	22.8	66.8	20.9	74.7	37.5	32.8
E	1	100.5	21.5	73.5	21.1	75.3	41.9	27.9
	2	100.5	21.0	75.7	21.1	75.3	42.3	27.5
	3	100.5	21.2	74.8	21.2	74.8	42.6	27.4
	$\bar{X}$	99.64	22.12[a]	70.69[a]	22.05	70.82	41.27[a]	28.60[a]
	S	1.32	1.68	7.08	1.66	7.33	1.88	2.34
	CV (%)	1.32	7.61	10.02	7.53	10.34	4.55	8.17

[a]Lab A Rep 2 and 3 for Sangamon and Lab A Rep 1, 2, and 3 for Vandalia results not included in calculations because of excessive (>500 ppm) sodium (Na) in post-procedure solutions.

TABLE 8—*Arsenic adsorption data for Sangamon paleosol, kaolinite clay, and the unaltered Vandalia till.*

			Sangamon		Kaolinite		Vandalia	
Lab	Rep	Initial Concentration, μg/mL	24-h Concentration, μg/mL	R_d, mL/g	24-h Concentration, μg/mL	R_d, mL/g	24-h Concentration, μg/mL	R_d, mL/g
A	1	101.3	81.2	4.95	87.3	3.21	86.9	3.31
	2	101.3	79.8	5.38	87.3	3.21	87.4	3.18
	3	101.3	81.4	4.89	87.3	3.21	87.2	3.23
B	1	101.7	81.5	4.96	87.7	3.19	88.4	3.01
	2	101.7	81.9	4.84	87.8	3.17	88.8	2.91
	3	101.7	82.7	4.59	90.0	2.60	89.2	2.80
C	1	101.4	82.3	4.64	85.8	3.63	88.5	2.92
	2	101.4	82.2	4.67	86.8	3.36	89.4	2.68
	3	101.4	82.0	4.73	86.0	3.58	88.5	2.92
D	1	100.4	79.5	5.25	85.9	3.37	86.6	3.19
	2	100.4	79.6	5.22	86.2	3.29	88.0	2.82
	3	100.4	79.4	5.28	86.6	3.19	87.6	2.92
E	1	99.8	81.7	4.43	86.5	3.07	87.3	2.86
	2	99.8	81.4	4.52	87.2	2.89	87.6	2.79
	3	99.8	80.9	4.67	86.8	3.00	87.6	2.79
	$\bar{X}$	101.0	81.16	4.86	87.01	3.20	87.93	2.95
	S	0.73	1.09	0.30	1.04	0.25	0.84	0.19
	CV (%)	0.73	1.35	6.15	1.20	7.95	0.95	6.37

TABLE 9—*Cadmium and arsenic adsorption data for the Sangamon paleosol, kaolinite clay, and the unaltered Vandalia till using 5 g solid to 100 mL solution or 10 g solid to 200 mL solution.*

Sorption, mL		Sangamon 24-h Concentration, μg/mL	Sangamon R_d, mL/g	Kaolinite 24-h Concentration, μg/mL	Kaolinite R_d, mL/g	Vandalia 24-h Concentration, μg/mL	Vandalia R_d, mL/g
		A. CADMIUM SORPTION: INITIAL CONCENTRATION 98.4 μG/ML					
5 g/100	1	21.0	73.7	21.3	72.4	39.8	29.4
	2	20.7	75.1	21.1	73.3	39.9	29.3
	3	20.7	75.1	21.0	73.7	40.0	29.2
	$\bar{X}$	20.8	74.6	21.1	73.1	39.9	29.3
10 g/200	1	21.1	73.3	23.6	63.4	39.7	29.6
	2	21.0	73.7	23.7	63.0	40.5	28.6
	3	21.0	73.7	23.5	63.7	40.7	28.4
	$\bar{X}$	21.0	73.6	23.6	63.4	40.3	28.9
		B. ARSENIC SORPTION: INITIAL CONCENTRATION 104.1 μG/ML					
5 g/100	1	80.2	6.0	85.9	4.2	89.5	3.3
	2	81.1	5.7	85.8	4.3	89.1	3.4
	3	81.5	5.5	86.1	4.2	88.3	3.6
	$\bar{X}$	80.9	5.7	85.9	4.2	88.9	3.4
10 g/200	1	80.6	5.8	85.9	4.2	89.0	3.4
	2	80.3	5.9	85.8	4.3	88.3	3.6
	3	80.7	5.8	85.9	4.2	88.3	3.6
	$\bar{X}$	80.5	5.8	85.9	4.2	88.5	3.5

similar manner. Each of the R_d means $\bar{X}$ and each analysis (Table 9) were treated as a possible outlier according to ASTM D 2777. From this analysis, it was found that none of the intralaboratory results (Table 9) could be discarded as being statistically invalid. Therefore it was concluded that there was no adverse effect because of varying the solid mass as long as the soil:solution ratio remained constant at 1:20. The variation in the mass of solid should be confined to masses between 5 and 70 g, since that was the range of testing.

Summary of Results

The results of the analyses and tests presented in this paper demonstrated the ability of the procedure to yield reproducible R_d values with coefficients of variation generally less than 10% for a variety of geomedia. Intralaboratory tests, using reduced masses, yielded data that were not statistically different from interlaboratory tests using larger soil masses.

Because of the nature of the test, a bias determination is not possible. This is predicated upon the fact that there is no independent means of determining a "true R_d," and also there is no standard soil. A precision statement, other

than the limited one presented in the procedure, is probably not feasible since the precision of the data would depend upon the homogeneity of the geomedia, precision of analysis, and the constituent of interest. However, it is felt that the precision of a R_d measurement for a species that meets the criteria of being stable and nonvolatile should yield a percent CV within the range established for arsenic and cadmium by the round-robin testing. It is believed that the procedure will be useful for stable inorganic compounds and for stable nonvolatile organic species. However, the effects of biodegradation, photodegradation, and hydrolysis should be addressed before this procedure can be used for studies of organic solutes. The method is not considered reliable for volatile chemical constituents and should not be used for this class of solutes.

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APPENDIX

Draft Method for 24-h Batch-Type Distribution Ratio (R_d) for Contaminant Adsorption by Soils and Sediments[4]

1. Scope

1.1 The method describes a procedure for determining the ability of an unconsolidated geologic material to attenuate solute concentrations in aqueous solutions.

1.2. This method is applicable in screening a large number of samples for their sorption ability for a given chemical constituent from aqueous solution.

1.3 While this procedure may be applicable to both organic and inorganic constituents, care must be taken with respect to the stability of the particular constituents and their possible losses from solution by such processes as degradation by microbes, light, or hydrolysis. This method should not be used for volatile chemical constituents.

[4]This method is under the jurisdiction of ASTM committee D-34 on Waste Disposal and is the direct responsibility of Subcommittee D-34.02 on Physical and Chemical Characterization. The method is currently under development by ASTM Committee D-34 and is not a full concensus method at the time of this publication.

1.4 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 ASTM standards:

- D 1129 Definitions of Terms Relating to Water
- D 1193 Specification for Reagent Water
- D 2216 Method of Laboratory Determination of Water (Moisture) Content of Soils, Rock, and Soil-Aggregate Mixtures
- D 3370 Practices for Sampling Water
- D 3987 Method for Shake Extraction of Solid Waste with Water

3. Summary of Method

3.1 Distilled water, natural waters, leachates, or other aqueous solutions containing a known concentration of a solute are mixed with a known amount of unconsolidated geologic material (geomedia) for 24 h. Changes in solute concentrations are used to calculate a distribution ratio R_d.

4. Terminology

4.1 Definitions—For definition of terms used in this method refer to ASTM D 1129.

4.1.1 Unconsolidated geologic material (geomedia)—a loosely aggregated solid natural material of geologic origin (for example, soil, sediment, till, and so forth).

4.1.2 Sorption—Depletion of an amount initially present in solution.

4.1.3 Solute—Chemical species (for example, ion, molecule, and so forth) in solution.

4.1.4 Sorbate—Chemical species sorbed by a sorbent.

4.1.5 Sorbent—A substance that sorbs the solute from solution (for example, soil, sediment, till, and so forth).

4.1.6 Sorption Affinity—The degree to which sorption occurs by a geomedia.

4.2 Description of Terms.

4.2.1 Distribution Ratio R_d—The concentration of sorbate, in μg/g, divided by the concentration of solute in μg/mL.

5. Significance and Use

5.1 This method is meant to allow for a rapid (24 h) index of a geomedia's sorption affinity for given chemicals or leachate constituents. A large number of samples may be run using this method to determine a comparative ranking, based upon amount of chemical sorbed per gram of geomedia, or by various geomedia. The 24-h time is used to make the test convenient and also to minimize microbial degradation that may be a problem in longer timed procedures. Because of this time constraint, the final (24-h) concentration should not be confused with that of an equilibrium or steady state concentration.

5.2 While this method may be useful in determining 24-h R_d values for nonvolatile organic constituents, it has only been tested for the nonvolatile, inorganic species, arsenic and cadmium. However, the procedure is believed to be useful for all stable and nonvolatile inorganic and organic constituents. This method is not considered appropriate for volatile constituents.

5.3 The 24-h time limit may be sufficient to reach a steady state R_d. However, to report this determination as a steady state R_d, the relevant time studies must be carried out to document the development of steady state conditions.

5.4 If this method is to be used as a basis for studies of R_d at greater than the prescribed time, proper controls must be implemented to account for possible microbial degradation or assimilation of the species in question.

6. Interferences

6.1 When dealing with solutes of unknown stability, care must be taken to determine if hydrolysis, photodegradation, microbial degradation, oxidation-reduction (that is, Cr^{3+} to Cr^{6+}), or other physicochemical processes are operating at a significant rate within the time frame of the procedure. The stability and hence loss from solution may affect the outcome of this procedure if the aforementioned reactions are significant.

7. Apparatus

7.1 Agitation Equipment—The agitation equipment to be used is the NBS rotating tumbler [5].

7.2 Phase Separation Equipment—A filtration apparatus made of materials compatible with the solutions being filtered and equipped with a 0.45-μm pore size membrane filter or a constant temperature centrifuge capable of separating particles with diameters greater than 0.1 μm (see Section 9). If organic compounds are being measured, the filtration apparatus, centrifuge tubes, and so forth should be compatible with the compounds being measured (that is, glass or stainless steel).

7.3 Containers—Round, wide-mouth bottles compatible with the NBS tumbler and of composition suitable to the nature of the solute(s) under investigation and the analysis to be performed will be used. For nonvolatile inorganic constituents, high-density linear polyethylene bottles should be used with the size of the bottle dictated by sample size, and the need for the solution to occupy 70 to 80% of the container volume (that is, 125-mL, 250-mL, or 2-L bottles for sample sizes of 5, 10, or 70 g, respectively). For nonvolatile organic constituents, Teflon®, glass bottles, or stainless steel containers with water tight closures made of chemically inert materials should be used with size requirements being the same as for nonvolatile inorganics. Containers should be cleaned in a manner consistent with the analyses to be performed. Samples of the solutions to be analyzed should be stored in similar chemically compatible bottles.

8. Reagents

8.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 Purity of water—Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water, Specification D 1193.

9. Procedure

9.1 Geomedia samples are spread out on a flat surface, no more than 2 to 3 cm deep, and allowed to air dry for 7 days or until constant weight is achieved (do not oven dry).

9.2 After the sample has air dried, it is passed through a 2-mm screen sieve. Large aggregates are to be crushed, without grinding, using a clean mortar and a rubber-tipped pestle.

9.3 Mix the sieved material until the sample is homogeneous. Use a riffle splitter, or other unbiased splitting procedure, to obtain subsamples of appropriate size.

9.4 Remove subsamples and determine the moisture content of the air-dried sample (refer to ASTM D 2216).

9.5 Determine the mass of geomedia sample, corrected for moisture content. Determination of air dry soil mass equivalent to the desired mass of oven-dried soil

$$A = Ms\,[1 + (M/100)]$$

where

A = air dry soil mass,
Ms = mass of oven-dried soil desired, and
M = percent moisture.

9.6 Place between 5 and 70 g (oven dried basis) of the weighed air dry sample into the appropriate container.

9.7 Add to the container an amount of solute solution necessary to yield a 1:20 soil-to-solution ratio. This is determined on the oven-dried basis. Determination of solution volume needed per sample for a soil-to-solution ratio of 1:20

$$V = (Ms \times 20)/\rho$$

where

ρ = density of solution, g/cm^3,
V = volume of solution per sample, cm^3, and
Ms = mass of soil to be used (oven-dry basis), g.

9.8 Retain a separate, appropriately preserved aliquot of the initial solute solution for analysis.

9.9 Close the container and place it on the NBS rotating tumbler.

9.10 Agitate continuously for 24 $\pm$ 0.5 h at 29 $\pm$ 2 rpm at room temperature (22 $\pm$ 5°C).

9.11 Open the container. Note the temperature of the solution and any changes in the sample or solution (that is, color, odor, and so forth).

9.12 Separate the solution phase from the majority of the solid phase by decantation.

9.13 Filter the solution phase through a 0.45-μm pore size membrane filter (see Section 7.2), or centrifuge a 50-mL subsample at the predetermined rate of rotation and time for the centrifugation equipment employed at constant temperature (the temperature recorded after 24 h)

$$t = 9/2\left(\frac{n}{\omega^2 r_p^2\,(\rho_p - \rho)}\right)\ln(R_b/R_t)$$

where

$\omega^2 = [4\pi^2(\text{rpm})^2/60]$ = angular velocity,
r_p = particle radius, cm,
n = viscosity of water (8.95×10^{-3} g/s · cm at 25°C),
ρ_p = particle density,
ρ = density of solution,
rpm = revolutions per minute,
R_t = distance from center of centrifuge rotor to top of solution in centrifuge tube, cm,
R_b = distance from center of centrifuge rotor to bottom of centrifuge tube, cm, and
t = time, min.

To remove particles >0.1 μ in radius and 2.65 g/cm^3 density from solution

$$t = \left(\frac{2.22 \times 10^{10}}{(\text{rpm})^2}\right) \ln(R_b/R_t)$$

NOTE—If filtration is used, the affinity of the filtration membrane for the solute must be evaluated. Failure to do so may lead to erroneous results.

9.14 After a clear solution has been obtained, place an aliquot in an appropriate container (see Section 7.3) and analyze or store in a refrigerator at 4 ± 2°C.

9.15 Each geomedia sample is to be subjected to the procedure in three or more replicates. The number of blanks to be carried through all steps of the procedure should be a minimum of 5% of the total number of geomedia samples, but not less than three.

10. Calculations

10.1 Calculate the distribution ratio

$$R_d = [(A - B)V/(Ms)B]$$

where

A = initial concentration of the solute defined as the mean concentration of the blanks, μg/mL,
B = final concentration of the solute after 24 h in contact with the geomedia, μg/mL,
V = volume of solution used, mL,
Ms = mass of soil expressed on an oven-dried basis, g, and
R_d = distribution ratio, mL/g.

11. Reporting

11.1 The R_d value must be clearly marked as a nonequilibrium 24-h distribution ratio.

12. Precision and Bias

12.1 The testing of this method was conducted as an interlaboratory round robin at a soil-to-solution ratio of 1:20 using 70.0 g of soil. Intralaboratory testing using a

TABLE 10—*Summary of interlaboratory testing for the 24-h batch-type* R_d *determination.*[a]

Initial Concentration, µg/mL	Soil 1 10	Soil 1 200	Soil 2 100	Soil 3 100	Soil 4 100
		CADMIUM (AS $CdCO_3$			
$\bar{X}$ R_d, mL/g	1568	96.3	69.50	69.74	28.94
SD, mL/g	156	6.32	±7.73	±7.87	±2.64
CV (%)	9.95	6.56	11.13	11.29	9.14
N	12	12	10	12	9
		ARSENIC (AS KH_2AsO_4)			
$\bar{X}$ R_d mL/g	15.42	2.75	4.95	3.25	2.99
SD, mL/g	0.92	±0.85	±0.27	±0.26	±0.20
CV (%)	5.99	30.9	5.53	7.88	6.52
N	12	12	12	12	12

[a]Soil 1: Catlin silt loam. Soil 2: Sangamon paleosol. Soil 3: Kaolinite clay. Soil 4: Vandalia till, unaltered phase.

1:20 soil-to-solution ratio was carried out with no significant loss of precision for soil masses of 5.00, 10.0, and 70.0 g. Therefore, it is specified that the soil-to-solution ratio be 1:20 with the working mass of soil (on an oven-dry basis) between 5 and 70 g.

12.2 Precision.

12.2.1 The precision of this test is limited by the ability to obtain a homogeneous sample of geomedia, and the precision of the various methods used to carry out the procedure (that is, mass determinations, initial and 24-h concentration of constituents).

12.2.2 A comprehensive overall precision statement, covering all species, is not feasible. Interlaboratory testing of this procedure, using cadmium and arsenic as sorbates, with five independent laboratories, indicated that a coefficient of variation of less than 10% is obtainable.

12.2.3 A summary of interlaboratory testing for the 24-h batch-type R_d determination is shown in Table 10.

12.3 Bias—A determination of the bias for this procedure is not possible since no standard soil or alternate technique exists.

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Evaluation of Paint Filter Test Method to Determine Free Liquid in Waste Samples

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ABSTRACT: This paper presents the results from a round-robin testing program to evaluate the paint filter test method developed by the U.S. Environmental Protection Agency (EPA) to determine whether a waste contains "free" liquid. Regulations prohibiting disposal of waste containing "free" liquids in landfills were the impetus for developing the test method. Six laboratories performed the paint filter test on four waste samples to determine (1) whether the waste contained "free" liquid and (2) the percent "free" liquid released by the waste. The four waste samples were from two wastes; one waste was mixed with three different amounts of water to provide three waste samples.

The results show a large variance between the laboratories. The large variance is attributed mainly to sample preparation. The participating laboratories noted two other major problems with the test: (1) separation of the mesh from the cardboard filter holder during testing and (2) differences in filter design, which could influence test results.

KEY WORDS: waste testing, hazardous waste, industrial wastes, waste treatment, liquid waste, solid waste

The purpose of this paper is to present the results of round-robin testing performed by six laboratories to evaluate a test method developed by the U.S. Environmental Protection Agency (EPA) to determine whether a waste contains "free" liquid. The impetus for evaluating this test was regulations developed by the U.S. EPA, which sought to limit liquids placed in landfills by prohibiting disposal of wastes containing "free" liquids [*1*].

The basis for this regulation was the increasing evidence of ground-water contamination by landfill leachate. One means of limiting leachate entering the ground-water system (and thus reducing ground-water contamination

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from landfills) is reducing the amount of leachate generated; and one of the most obvious means of limiting leachate production is through eliminating liquids placed in landfills. Thus, regulations were promulgated by the U.S. EPA to prohibit placing liquid wastes and solid wastes containing "free" liquid in landfills [*1*].

However, the regulations did not include a method for evaluating whether a waste contained "free" liquids. Various methods for determining "free" liquid were evaluated by the U.S. EPA. These methods included using an inclined plane, lab press filtration unit, graduated cylinder test, sieve series, and paint filter [*2*]. Of the test methods evaluated, the one which seemed most promising was the paint filter test. The report submitted to the U.S. EPA by SMC Martin, Inc., [*2*] evaluating various test methods, stated that the paint filter test was one of three tests that provided accurate reproducible data that could be used on a pass/fail basis for "free" liquid determination. This test met the criteria of a quick, easy, and inexpensive test that could be performed by a landfill operator. In addition, the report also recommended that one of the test methods that was evaluated should be selected for refinement and further testing [*2*].

Recognizing the need for developing a method to determine whether a waste contained "free" liquid, the physical analytical section of ASTM Subcommittee D34.02 on Physical and Chemical Characterization decided to evaluate the reliability of the paint filter test method by performing a round-robin test involving six laboratories and two wastes. The purpose of this paper is to present the results of the testing program.

Procedure

The paint filter test requires a minimum of equipment, a paint filter that can be obtained at any paint supply store, a funnel, a ring stand to support the filter, a graduated cylinder to record the amount of liquid released by the waste, and a watch glass to place on top of the waste. The test setup is shown in Fig. 1. The paint filter consists of a cardboard frame with a cotton mesh glued onto the cardboard frame.

A measured volume of waste (100 mL) is placed in the paint filter funnel with the watch glass placed on top of the waste. The waste is then allowed to freely drain for 5 min. If the waste releases any liquid it has failed the test and is said to contain "free" liquid.

In addition to the pass/fail determination of whether a waste contained "free" liquid, the test also includes a procedure to determine the percent of "free" liquid that can be released by the waste. After the 5-min draining period, the amount of water released is recorded, the waste is allowed to drain for an additional 15 min, and the total amount of liquid released is measured. If the change in the amount of liquid measured is less than 10% the test is terminated; if the change in the amount of liquid released is more than 10%

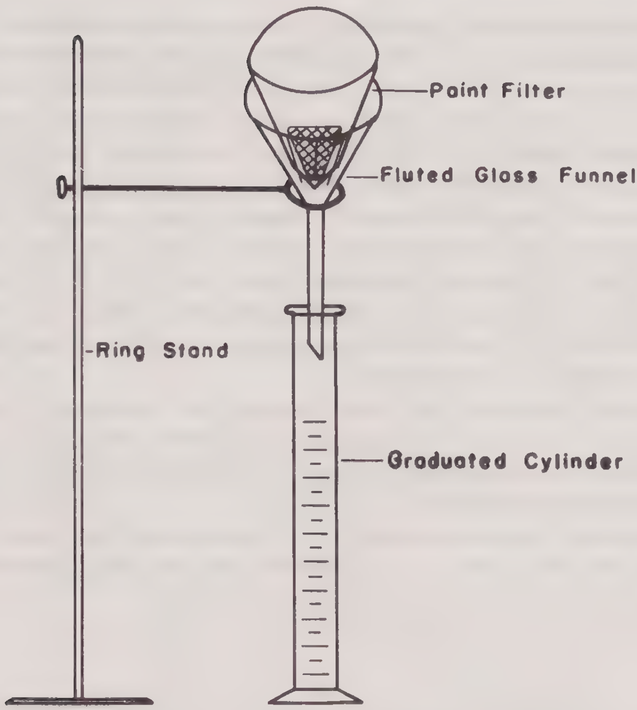

FIG. 1—*Paint filter test apparatus.*

the test is continued using 15-min time increments until the change is less than 10%. The test is terminated when the percent change between 15-min increments is less than 10% and the total liquid released by the waste is recorded.

The percent change is calculated using the equation

$$\text{percent change} = \frac{\text{current reading (mL)} - \text{proceeding reading (mL)}}{\text{proceeding reading (mL)}} \times 100$$

The percent "free" liquid released by the waste is calculated using the equation

$$\text{percent "free" liquid} = \frac{\text{total liquid phase (mL)}}{\text{sample size (mL)}} \times 100$$

In order to evaluate the paint filter test, two wastes were sent to each of the

six laboratories for testing. The two wastes were a sludge consisting of a mixture of bentonite powder and an unidentified alkaline waste supplied by the U.S. EPA and sawdust. The sludge was sent premixed to each laboratory, while the sawdust was sent in a dry form to each laboratory with instructions on preparing the waste for testing. The sawdust was chosen to provide a heterogeneous waste that could be tested at different moisture contents.

The sawdust was oven dried by each laboratory, then a weighed amount of sawdust mixed with a measured amount of distilled water to prepare a "waste" sample. The sawdust was dried in an oven at 105 ± 2°C for 24 h. Twenty grams of dried sawdust were mixed with three different quantities of distilled water: 80, 100, and 120 mL to prepare the "waste." No sample preparation was required for the sludge.

In addition to the wastes, each laboratory was sent eight paint filters, with instructions to purchase paint filters locally so replicate tests could be run on each waste sample, one test using the supplied paint filter, and one test using a locally purchased paint filter.

Each laboratory was also instructed to perform duplicate tests on each waste. With the four wastes, two paint filter types and duplicate tests, each laboratory was instructed to perform a total of 16 tests.

Results

All six laboratories reported no "free" liquid for the premixed waste sample of sludge using both the supplied filter and the locally purchased filter.

The results from the tests performed on the sawdust mixed with water are shown in Tables 1 through 3. Table 1 contains the tabulated data for the

TABLE 1—*Paint filter test results for sawdust mixed with 80-mL water.*

	Supplied Filter		Local Filter			
Laboratory	% Free Liquid Test 1	% Free Liquid Test 2	% Free Liquid Test 1	% Free Liquid Test 2	$\bar{x}$	s
1	0.0	0.0	0.0	0.0	0.0	0.0
2	1.8	5.5	1.7	3.4	3.1	1.8
3	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	5.3	1.3	0.0	1.6	2.5
5	0.5	...	5.0	...	2.8	3.2
6	6.7	...	2.0	...	4.4	3.3
$\bar{x}$	2.0[a]		1.3[a]		1.7[b]	
s	2.7		1.7		2.3	

[a]Mean and standard deviation of each filter type.
[b]Mean and standard deviation of total test results.

TABLE 2—*Paint filter test results for sawdust mixed with 100-mL water.*

	Supplied Filter		Local Filter			
Laboratory	% Free Liquid Test 1	% Free Liquid Test 2	% Free Liquid Test 1	% Free Liquid Test 2	$\bar{x}$	s
1	9.5	4.0	10.0	6.0	7.4	2.9
2	17.5	19.2	19.0	27.0	20.7	4.3
3	6.9	3.6	5.2	4.0	5.2	1.6
4	4.5	17.4	16.0	7.2	11.3	6.4
5	9.0	...	17.0	...	13.0	5.6
6	16.3	...	18.2	...	17.3	1.3
$\bar{x}$	10.0[a]		13.0[a]		11.9[b]	
s	6.2		7.6		6.8	

[a]Mean and standard deviation of each filter type.
[b]Mean and standard deviation of total test results.

TABLE 3—*Paint filter test results for sawdust mixed with 120-mL water.*

	Supplied Filter		Local Filter			
Laboratory	% Free Liquid Test 1	% Free Liquid Test 2	% Free Liquid Test 1	% Free Liquid Test 2	$\bar{x}$	s
1	18.5	15.0	15.0	16.0	16.1	1.7
2	36.0	32.0	37.0	39.0	36.0	2.9
3	12.5	13.5	14.5	12.9	10.5	6.2
4	35.0	31.5	43.5	37.5	36.9	5.1
5	6.0	...	24.0	...	15.0	12.7
6	36.2	38.8	38.6	36.7	37.6	1.3
$\bar{x}$	25.0[a]		28.6[a]		26.8[b]	
s	11.9		12.1		11.8	

[a]Mean and standard deviation of each filter type.
[b]Mean and standard deviation of total test results.

waste sample prepared by mixing 20 g of sawdust with 80 mL of water, Table 2 contains the tabulated data for the waste sample prepared by mixing 20 g of sawdust with 100 mL of water, and Table 3 contains the tabulated data for the waste sample prepared by mixing 20 g of sawdust with 120 mL of water.

The results show a large variance between laboratories for all three waste samples. The mean percent "free" liquid determined by all six laboratories for sawdust mixed with 80 mL of water was 1.7 with a standard deviation of

2.3. Using the Student's t distribution, the 95% confidence interval for the mean percent "free" liquid is between 0.6 and 2.8% "free" liquid. The mean percent "free" liquid determined by four out of the six laboratories is outside of the 95% confidence interval. The results for sawdust mixed with 100 and 120 mL of water are similar. The 95% confidence interval for the mean percent "free" liquid for sawdust mixed with 100 mL of water is between 8.7 and 15.1%; and for sawdust mixed with 120 mL of water the 95% confidence interval for the mean percent "free" liquid is between 17.0 and 36.6%. The mean percent "free" liquid calculated by four of the six laboratories was outside of the 95% confidence interval for sawdust mixed with 100 mL of water; while the mean percent "free" liquid calculated by five of the six laboratories was outside of the 95% confidence interval for sawdust mixed with 120 mL of water.

An analysis of the data for the supplied filter versus the locally purchased filter does not show any significant difference between the mean percent "free" liquid at the 95% confidence level for any of the three sawdust and water mixtures.

Discussion

The large variance between laboratories is attributed mainly to sample preparation. Both the way sample size was determined and the characteristics of the sawdust and water mixture contributed to large variations in the amount of the sample mixture tested by each laboratory.

The directions for determining the sample size called for measuring a known volume of the waste and placing it in the paint filter. Since the sawdust and water mixture was very compressible, the weight of a measured volume of the sample could vary by 100%, depending on how densely the sample was placed in the container used to measure the 100-mL of sample. A densely packed 100-mL sample of sawdust and water will contain more water than a loosely packed 100-mL sample, resulting in a higher percent "free" liquid determination for the more densely packed sample.

The results from Laboratory 6 demonstrate this effect. All laboratories were supplied the same weight of sawdust. Laboratory 6 reported they did not have enough sample to run duplicate tests for the sawdust and 80-mL water mixture or the sawdust and 100-mL water mixture. Laboratory 6 used most of the sawdust and water from mixtures they prepared using 20-g sawdust with 80- and 100-mL water to obtain one 100-mL sample for testing. Laboratories 1, 3, 4, and 5 were able to obtain two 100-mL samples from the same mixture.

The mean results from Laboratory 6 for samples prepared by mixing sawdust with 80-mL water and 100-mL water (Tables 1 and 2) were higher than all other laboratories except Laboratory 2. Laboratory 2 did not measure out a known volume of the waste; instead the entire mixture was placed in the paint filter. Thus, the results from Laboratories 2 and 6 for the samples pre-

pared by mixing sawdust with 80- and 100-mL water are higher than the other laboratories because the sample tested contained more of the sawdust and water mixture and therefore more water.

Another waste characteristic that may have also contributed to variance is the ability of the sawdust to absorb liquid. The waste preparation directions called for mixing a known weight of oven dried sawdust with a measured volume of water, then measuring a known volume of the mixture for the test. The procedure for mixing the dry sawdust and water was not specified. If the sawdust and water were rapidly mixed then placed in the paint filter, the mixture would release more liquid than if the mixture were mixed thoroughly and allowed to stand for half an hour before the test was performed. The tendency of the sawdust to absorb water with time was reported by two of the six laboratories.

Other problems in performing the test were also noted. These included separation of the mesh part of the filter from the cardboard filter holder and differences in filter design, which could influence test results. Two "standard" paint filters are available. One type of paint filter has an open mesh on the filter tip while the other has a small cardboard cone on the filter tip. The cardboard cone on the filter tip can hold several millilitres of liquid. The filter supplied to each laboratory had a cardboard cone on the tip. Laboratories 1 and 3 reported that the locally purchased filters had mesh on the tip of the filter while Laboratory 2 reported the purchased filter was identical to the supplied filter. The other laboratories did not specify whether there was or was not a difference between the purchased and supplied filters. The results do not indicate any difference between the mean percent "free" liquid determined using the supplied and purchased filters. However, the locally purchased filters were sometimes the same and sometimes different from the supplied filter, thus the difference between a filter with a cardboard cone and without a cardboard cone at the tip cannot be evaluated. It would be expected, though, that for determining percent "free" liquid on wastes with a low percent "free" liquid, the amount of liquid retained by the cone in the filter tip could influence results.

Separation of the filter mesh from the cardboard was a problem reported by three of the six laboratories. The water appeared to dissolve the glue used to attach the mesh to the cardboard.

Conclusions and Recommendations for Further Work

The results from the round-robin test to determine percent "free" liquid using a paint filter showed large variance between laboratories. Although the major factor contributing to the variance appears to be sample preparation, which could be improved, other problems with the test were also noted. The main problem, which would remain even with an improvement of sample preparation, involved the paint filter itself. Not only did the mesh separate

from the cardboard, but the design of a "standard" paint filter varied and could affect results.

The round-robin testing was performed during the summer of 1984. The reauthorization of the Resource Conservation and Recovery Act by Congress in the fall of 1984 amended the provisions relating to disposal of liquids in landfills [*3*]. The new provisions include the stipulation that the regulations "shall also prohibit the disposal in landfills of liquids that have been absorbed in materials that biodegrade or that release liquids when compressed as might occur during routine landfills operations" [*3*]. Given these stipulations, the definition of "free" liquids is expected to change to include liquids that could be released under pressures routinely encountered at the base of a landfill. Thus, a test to evaluate "free" liquids must also account for the effect of pressure. Since the paint filter test was developed for evaluating the release of liquids under normal atmospheric conditions, a new test will be needed. No further work is planned by the physical analytical section of ASTM Subcommittee D34.02 on the paint filter tests. Instead, the physical and analytical section of Subcommittee D34.02 is currently examining and evaluating tests that can be used to determine the release of "free" liquid under pressures expected at the base of a landfill.

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Laboratory and Waste Management for Safety and Regulatory Compliance

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ABSTRACT: Federal, state, and local rules and regulations often affect even small generators of waste materials. Chemical laboratories are perfect examples with a need to develop procedures to dispose of small quantities of laboratory wastes in a safe and environmentally acceptable manner.

Recognizing a need, the ASTM D-34 committee on waste disposal created its Subcommittee D34.01.05 on Sample Disposal with the direct responsibility for developing guidelines for laboratories. While it was impossible to address the disposal of all wastes from all types of laboratories, the guidelines did address the more common laboratory waste streams. They are applicable, but not limited to, analytical chemistry, process control, and research or life science laboratories.

The recommended guidelines for disposal cover the following topics: (1) the classification of waste for shipping and manifesting by common or generic name and by Department of Transportation requirements; (2) the segregation of wastes for recovery, pretreatment, or disposal; (3) the procedures for recovery of materials, or to render them nonhazardous and amenable for landfilling or in-house disposal, or to prepare them for disposal in authorized chemical disposal sites; and (4) the designation of a specific recovery or pretreatment and disposal method for each type of waste.

KEY WORDS: wastes, laboratory, classification, treatments, disposal

The laboratory manager faces two responsibilities regarding waste labora-

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tory chemicals or samples, that of providing a safe workplace environment while complying with regulatory directives concerning hazardous wastes. These responsibilities are not necessarily incompatible but may present a dilemma in material organization and handling.

Recognizing the problem, ASTM has developed a proposed guide for managers. This guide is intended to provide the chemical laboratory manager with procedures to safely and in an environmentally sound manner dispose of small quantities of laboratory waste. It is applicable to laboratories that generate small quantities of chemical or toxic wastes. Generally, such tasks would include, but not be limited to, analytical chemistry, process control, and research or life science laboratories. It would be impossible to address the disposal of all waste from all types of laboratories. This approach is intended to address the more common laboratory waste streams.

Laboratories rarely generate or handle large volumes of hazardous substances. However, the safe handling and disposal of these substances are impaired by diversity, toxicity, high hazard risks, and contemptuous familiarity. With the promulgation of the Resource Conservation and Recovery Act (RCRA) of 1976, more attention is being given to the proper handling and disposal of such materials. Top laboratory personnel must be responsible for waste disposal and must review the RCRA guidelines, in particular, the definition of a hazardous waste, the specific substances listed as hazardous, generator requirements and exclusions, and proper shipping and manifesting procedures. Because many laboratory employees could be involved in the proper (and improper) treatment and disposal of laboratory chemicals and samples, it is suggested that a safety and training program be designed and presented to all regarding procedures to follow in the treatment and disposal of designated laboratory wastes.

If practical and economically feasible, it is, of course, recommended that all laboratory waste be either recovered, reused, or disposed of in-house. The disposal of laboratory samples, especially those received in large numbers of quantities from a specific source, can often be accommodated by returning the material to the originator, so he can combine them with larger quantities for recycling or disposal. However, should this not be the case, other alternatives are presented. The ASTM guide is intended as only a suggested organized method for classification, segregation, and disposal of chemical laboratory waste.

Even though the small quantity generator exclusion (40 CFR 261.5) may apply to laboratories, the professional laboratory supervisor and his employers must balance the importance of protecting human health and the environment from the adverse impact of potential mismanagement of small quantities of hazardous waste, with the need to hold the administrative and economic burden of management of these wastes under RCRA within reasonable and practical limits.

Classification of Laboratory Waste

The individual responsible for classification and segregation must be familiar with the waste's chemical, physical, and hazardous properties. If the waste is ultimately to be disposed of off-site, it must be segregated and classified according to defined Department of Transportation (DOT) hazard classification, as specified in the DOT hazardous materials regulations (49 CFR 172).

The chemical waste may be segregated into the following waste types:

1. Trash, Inert Chemicals—nontoxic, nonreactive, nonignitable, noncorrosive solids as per RCRA guidelines.
2. Weak aqueous acid solutions (less than 10% weight) and related compounds.
3. Weak aqueous alkaline solutions (less than 10% weight) and related compounds.
4. Concentrated aqueous acid solutions and related compounds.
5. Concentrated aqueous alkaline solutions and related compounds.
6. Flammable (flash point, closed cup less than 60°C [140°F]), nonhalogenated organic solvents and related compounds.
7. Flammable halogenated organic solvents and related compounds.
8. Nonflammable nonhalogenated organic solvents and related compounds.
9. Nonflammable halogenated organic solvents and related compounds.
10. Organic acids.
11. Organic bases.
12. Inorganic oxidizers, peroxides.
13. Organic oxidizers, peroxides.
14. Toxic—heavy metals.
15. Toxic—poisons, herbicides, pesticides, and carcinogens.
16. Aqueous solutions of reducing agents and related compounds.
17. Pyrophoric substances.
18. Hydrophoric substances.
19. Cyanide, sulfide, and ammonia bearing waste.
20. Explosive materials.
21. Radioactive materials.
22. Infectious Waste—life science laboratories.
23. Infectious Waste—hospitals.
24. Water soluble waste of unknown origin or properties.
25. Water insoluble waste of unknown origin or properties.
26. Empty containers.
27. Asbestos or asbestos containing waste.
28. Contaminated lab ware, trash.
29. Polychlorinated biphenyls (PCBs).

Pretreatment and Recovery Methods

Several methods may be employed for the recovery or pretreatment of waste in the laboratory. All persons using chemicals in the laboratory must be aware of the toxic or hazardous properties of the substance(s) used, including consideration of the toxic properties of possible reaction products. In incorporating the following procedures, one must examine the possible hazards associated with each.

Recovery, Reuse

Consideration should be given to distillation for the recovery of larger volumes of solvents. Many laboratories have systems for the recovery and reuse of mercury. Other recovery methods, such as precipitation or crystallization, may be practical.

Dilution

Many laboratory chemical wastes can be diluted to an extent to allow disposal to the sewer system. Strong acids and bases should be diluted to pH 3 to 11 for this purpose. Some solutions of water soluble flammable solvents can be diluted enough to render them nonflammable. Small amounts of various heavy metal compounds may be diluted to an extent to not pose a hazard to a sewer system. Consult the local wastewater treatment facility for acceptable guidelines.

Neutralization

Strong acids and bases can carefully be neutralized to pH 3 to 11 to render them less hazardous for disposal.

Oxidation

Compounds, such as sulfides, cyanides, aldehydes, mercaptans, and phenolics, can be oxidized to less toxic and less odoriferous compounds.

Reduction

In addition to oxidizers and peroxides, various organic chemicals and heavy metal solutions can be reduced to less toxic substances. Aqueous waste containing hexavalent chromium may be reduced to trivalent using reducing agents such as bisulfide and ferrous sulfate. Mercury, lead, and silver may be removed from aqueous streams by the process of reduction/precipitation. Organo-lead compounds can be removed by the same type processes. The result-

ing concentrated heavy metal waste can be containerized and disposed of at an authorized hazardous waste management facility.

Controlled Reactions/Processes

Other methods for reducing the hazardous properties of waste will involve processes specific to particular waste generated by the laboratory. To be practical, the waste would have to be of sufficient volume and, for safety purposes, the process would need to be carefully studied and the resulting products identified. Examples may include evaporation, filtration, ion exchange, carbon absorption, solvent extraction, hydrolysis, ozonolysis, and electrolysis.

Disposal Methods

The disposal methods identified are the most applicable for the laboratory management decision-making process. They can be classified into seven categories.

Containerization (Dumpster)

This method should be used only in the disposal of inert laboratory solid waste. Each institution should have a procedure for handling solid waste to include classification, segregation, and collection. Materials disposed of in this manner must be suitable to sanitary landfill disposal and must be of no threat to the personnel picking up the waste. Many materials disposed of in this manner by laboratories may be regulated by local authorities.

Disposal to the Sewer System

Many laboratory chemicals, with or without pretreatment by one or more of the above prescribed methods, are amenable to sewer disposal. Generally, local regulations govern the concentrations and types of chemicals that may be let to a sewer. Laboratory supervisors must familiarize themselves and their coworkers with these regulations. In addition to the statements made earlier regarding dilution and neutralization, highly toxic, malodorous, or lachrymatory chemicals should not be disposed of down the drain. Laboratory drains are usually interconnected, and a substance that goes down one sink may arise as a vapor from another. Additionally, the comingling of waste from different sources in the sewer system may present definite hazards, the sulfide poured down one drain may contact an acid poured into another. Some simple reactions, such as ammonia plus iodine or silver nitrate plus ethanol, may produce explosions. Laboratory supervisors must be aware of the type of chemical disposed in this manner so that the risk of potential laboratory accidents is reduced.

Incineration, Solvent Recovery

Waste solvents free of solids and corrosive or reactive substances should be collected, segregated, and containerized. Because of the fact that some incineration or solvent recovery sites will not handle chlorinated solvents, it is often necessary to segregate into two or three types of waste solvents. In addition to solvent recovery techniques, which may be employed in the laboratory, some of these materials may be disposed in-house by mixing with fuel oils for combustion in process boilers, power generators, and so forth. Additionally, outside disposal firms may be contacted for disposal, but they generally are less interested in handling small volume waste streams, particularly if inconsistent in composition. The laboratory supervisor should be aware of the chemicals collected, and insure that incompatible materials are not comingled.

Lab Pack

EPA regulations allow the disposal of small containers of hazardous waste (liquids and solids) if packed in drums in secure or specially permitted landfills.

Each chemical is to be identified by its generic or common name, the quantity, and the DOT hazard classification. All chemicals are to be segregated and packaged according to the following classification, poisons, oxidizers, flammables, corrosive-acids, and corrosive-alkalies.

Many chemicals that are similarly classified will react; for example, concentrated solutions of nitric acid mixed with acetic acid can cause spontaneous ignition. Therefore, an employee of the waste generator, familiar with the chemicals and their respective hazards, is to be responsible for not only segregation, but also the documentation and the following packaging operation: Compatible materials, of the same classification, are to be packaged in tightly and securely sealed inside containers of the size and type specified in the DOT hazardous materials regulations (40 CFR 173, 178, 179), if those regulations specify a particular inside container, and placed in DOT approved open-top metal drums.

Vermiculite or another inert material is to be placed around the original waste containers to avoid breakage and to act as an absorbent should any breakage or leakage occur. The chemicals are to be equally distributed within the drum with not less than an equal volume of absorbent. The drums must be completely filled and properly sealed.

A list detailing the contents of each drum, including the chemicals' common or generic names, the DOT hazard classes, quantities of each, and any pertinent comments, must be available for completion of manifesting purposes and for the disposal firm.

Solidification

In addition to the lab pack, an alternate drum disposal method involves the solidification of compatible liquid chemical waste with vermiculite or a suitable solidification agent such as diatomaceous earth or clay. A suggested procedure is as follows: a DOT approved open-top metal drum (17H) containing a free-standing liner is filled to approximately one-third with the absorbent. The liquid waste is then carefully poured into the absorbent, mixed, and allowed to stand. The liquid waste may need pretreatment (for example, neutralization, reduction, and so forth) to render it compatible with the solidification agent. The remainder of the drum is then filled in the same manner. An extra layer of dry absorbent (about 5.08 cm [2 in.]) is added to top off the drum to contain any free liquid that may surface in transporting or handling. The drum must be completely full, contain only solids, and be properly sealed and labeled.

A list detailing the contents of each drum, including the chemicals' common or generic names, the DOT hazard classes, quantities of each, and any pertinent information, must be available for manifestating purposes and for the disposal firm.

Waste Exchange

One may evaluate the possibility of using a waste exchange for specific waste generated by a laboratory, especially if large quantities are produced. One laboratory's unused chemicals or waste may be another laboratory's reagent, with possibly only minor pretreatment methods.

Summary

It is possible to handle laboratory materials and chemicals in a manner that provides a safe work environment and complies with regulatory requirements. This is possible when (1) wastes are segregated and processed for potential recovery, pretreatment or disposal or both and (2) procedures are implemented for DOT and EPA approved shipping for ultimate disposal.

It should be noted that the ASTM proposed guidelines for disposal of laboratory chemicals and samples also addresses disposal in cooperation with the local fire or police department, radioactive waste disposal, and the management of infectious and PCB wastes.

Additionally, methods for disposal of contaminated lab ware and trash, asbestos and asbestos containing materials, empty containers and unknown chemical wastes are mentioned.

The guidelines also contain listing pretreatment and disposal methods for each class of waste shown in Table 1.

TABLE 1—*Pretreatment and disposal methods.*

Waste Types	Pretreatment Methods	Disposal Methods
Trash	. . .	containerization
Weak acids	dilution, neutralization	sewer, solidification
Weak bases	dilution, neutralization	sewer, solidification
Concentrated acids	dilution, neutralization	sewer lab pack solidification
Concentrated bases	dilution, neutralization	sewer lab pack solidification
Flammable nonhalogen solvents	. . .	incineration lab pack solidification
Flammable halogen solvents	. . .	incineration lab pack solidification
Nonflammable, nonhalogen solvents	. . .	incineration lab pack solidification
Nonflammable, halogen solvents	. . .	incineration lab pack solidification
Organic acids	neutralization	sewer incineration lab pack
Organic bases	neutralization	sewer incineration lab pack
Inorganic oxidizers	dilution, reduction	sewer lab pack
Organic oxidizers	dilution, reduction	sewer lab pack
Toxic metals	dilution, reduction	sewer lab pack solidification
Toxic organics	dilution, oxidation	sewer lab pack solidification
Aqueous solutions of reducing agents	dilution, oxidation	sewer lab pack solidification
Pyrophorics	. . .	fire or PD
Hydrophorics	. . .	fire or PD
Cyanide, sulfide, or ammonia containing waste	dilution, oxidation	sewer lab pack
Explosives	. . .	fire or PD
Radioactive	. . .	special waste refer to guide
Infectious wastes	sterilization, disinfection; refer to guide	incineration lab pack
PCBs	. . .	refer to guide

Future Developments

The ASTM Task Group D34.01.05 will review applicable regulations concerning the management of laboratory waste and incorporate necessary changes in future revisions of the guide. It is the intent of the committee to keep the guide updated and complete as possible.

Future revisions may also include new technologies as they become available concerning the treatment and disposal of laboratory waste, which will be reviewed and evaluated by the Task Group.

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A New Look at Storage of Hazardous Materials and Wastes

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ABSTRACT: In response to the need for improved information concerning hazardous materials/wastes in a storage environment, the Hazardous Materials Technical Center (HMTC) reviewed the definition of hazardous materials and applicable regulations and developed a storage classification scheme for packaged commodities. Seventy-seven final storage compatibility groups were developed from 12 major areas defined by regulation. To arrive at this scheme, HMTC combines Department of Defense (DOD) hazardous material storage/disposal methods, industry-based storage/disposal guidelines, and survey/analysis of regulations affecting the public and military sectors (for example, Department of Transportation, Occupational Safety and Health Administration, Environmental Protection Agency, Nuclear Regulatory Commission). Tables provide major definitions, a priority list of materials for multiple hazard, and major groupings of hazardous materials. Figures illustrate the development of the 77 final compatibility groups.

KEY WORDS: flammability, corrosivity, oxidizing, radioactivity, explosive nature

The term "hazardous" has been applied to materials and wastes because those so-identified items have been shown or thought to be detrimental to health and environment. Obviously, not all such hazards are the same, and not all items present the same degree of hazard. Also, not all hazardous materials/wastes are hazardous in all environments. For example, a truck containing more than 2 gal (8 L) of gasoline is not considered a hazard, unless you are to transport it. Then Department of Transportation (DOT) regulations spec-

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ify that it is hazardous and must be so identified. A drum of heavy metal laden sludge is only hazardous for disposal operations, not occupationally and not for transportation. Unfortunately, we have often transferred the rating of hazardous from one medium to another without fully evaluating whether or not the item is hazardous in the new medium.

This paper represents a summary of the procedures and findings Dynamac Corporation undertook for the Department of Defense. Before embarking upon this new look, we must look at the storage environment.

The storage environment is very diverse. It can consist of open storage areas (no construction and earthbase), special base open storage (no construction and concrete or asphalt base), open shed storage (earth or special base with open sided, roofed construction), partially closed shed storage (open shed storage with one to three sides enclosed), shed storage, and so on up to warehouses. With warehouses, we generally envision loading docks and ramps, fire protection systems, and concrete or wood floors.

For the purposes of this evaluation, only the storage of packaged commodities was involved. These ranged in size from small vials to 55-gal (208-L) drums. Bulk storage was not addressed.

Initial Review

The first task undertaken was a review of the following hazardous/toxic substances laws, regulations, and definitions:

1. Clean Air Act
2. Federal Food, Drug, and Cosmetic Act
3. Flammable Fabrics Act
4. Federal Hazardous Substances Act
5. Clean Water Act
6. Poison Prevention Packaging Act
7. Safe Drinking Water Act
8. Toxic Substances Control Act
9. Consumer Product Safety Act (CPSA) 16 CFR 1500 series
10. Nuclear Regulatory Commission (NRC) 10 CFR
11. Hazardous Materials Transportation Act (HMTA) (DOT) 49 CFR
12. Resource Conservation and Recovery Act (RCRA) 40 CFR
13. Occupational Safety and Health Act (OSHA) 29 CFR
14. American National Standards Institute (ANSI), American National Standard for the Precautionary Labeling of Hazardous Industrial Chemicals (ANSI 2 129.1-1976)
15. National Fire Protection Association (NFPA) Standards
16. Compressed Gas Association (CGA) Standards
17. Bureau of Explosives (BOE), Association of American Railroads Standards

18. Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) 40 CFR
19. International Air Transport Association (IATA) Regulations

After reviewing the regulations, a pattern was identified that led to the selection of the following 12 categories of hazardous materials:

- Flammables
- Corrosives
- Oxidizers
- Compressed gases
- Radioactive materials
- Poisonous/infectious substances
- Organic peroxides
- Explosives
- Pesticides
- Other regulated materials
- Multiple hazard materials
- Personal hazard communication group materials

In addition to these categories, the following four conclusions were reached:

1. The Department of Transportation (DOT) recognized that the Nuclear Regulatory Commission's (NRC) primary concern is with radioactive materials and established the transportation and packaging criteria with the concurrence of NRC. It is recommended that DOT standards, as defined in 49 CFR, be utilized to determine which items present radioactive hazards. However, since NRC has primary regulatory responsibility under the law and was actively consulted by DOT, it is also recommended that NRC's 10 CFR Part 71 be used in cases where 49 CFR criteria are insufficient.

2. DOT also recognized that hazardous wastes and pesticides are among the Environmental Protection Agency's (EPA) primary concerns and sought EPA's recommendations for the development of criteria in those areas. The EPA's influence on the DOT criteria is clearly evident (for example, 49 CFR contains the reportable quantities (RQ) verbatum from EPA, the hazardous waste transportation instructions (ORM-E) were a joint EPA/DOT effort, and DOT included transportation descriptions for all EPA-controlled federal insecticide, fungicide, and rodenticide chemicals in its 49 CFR 101 table). Therefore, it is recommended that the EPA's 40 CFR be consulted in cases where the DOT criteria and standards for classification and definition wastes and pesticides are insufficient.

3. DOT established a specific category, ORM-D, for consumer commodities. In the industrial environment, compliance with the criteria established by the DOT, EPA, and the Occupational Safety and Health Administration (OSHA) more than adequately satisfies compliance with Consumer Product Safety Commission (CPSC) regulations for hazardous materials and toxic

substances. Thus, CPSC regulations, which are primarily oriented toward commodity consumers, were judged to have very little impact on day to day warehouse operations.

4. Criteria developed by the American National Standards Institute (ANSI) and the National Fire Protection Association (NFPA) are essentially the same as those developed by DOT and OSHA with some minor variances in terminology and hazard communications systems. In fact, OSHA and NFPA descriptions of flammables are nearly identical and are recommended for use. Use of the OSHA/NFPA criteria eliminates the communications problem among storage, fire department, and safety personnel regarding the hazards of commodities in storage in the event of an emergency.

As evidenced by the foregoing conclusions drawn from the review, the criteria promulgated by DOT and OSHA definitely have the greatest impact on day to day storage operations. It is recommended that the emphasis be placed on these two agencies' criteria in considering which commodities require specialized storage and handling. Additional reasoning behind this recommendation is as follows:

1. OSHA's Hazard Communication Program (which became effective 25 Nov. 1985), specifically states that labels affixed to hazardous commodities must not be in conflict with labels required by DOT under the Hazardous Materials Transportation Act. Therefore, a storage activity's primary means of identifying hazardous commodities is a label on the material, as specified by DOT/OSHA regulations.

2. The storage activity's secondary means of identifying hazardous or toxic materials will be from the shipping documentation when the material is received into the warehouses or from the Material Safety Data Sheet corresponding to the material. Guidelines for preparation and content of shipping documents and Material Safety Data sheets are promulgated by DOT, OSHA regulations, and the latest edition of Federal Standard 313B, respectively.

3. Both DOT and OSHA take the position that if their published criteria are not considered to have sufficient depth for a specific problem, they refer to the agency or organization with the most expertise. Both DOT and OSHA identify the source of the expertise; for example, DOT will state that the criteria for radioactive material in 49 CFR is in addition to, but not in lieu of, the requirements set forth by NRC in 10 CFR; or in referring to valves on cargo tanks in 49 CFR, DOT recommends obtaining flow formulas from the Compressed Gas Association or the Bureau of Explosives.

Development of Subcategories

Next we summarized the criteria from those identified activities and agencies considered to have the most influence in defining and regulating each of the 12 categories identified. For an example of the summary of definitions, refer to Table 1, which shows some of the definitions of corrosives.

TABLE 1—*Corrosivity definitions.*

Classification	Definition Criteria to Meet Classification	Regulation/Standard
Corrosive	Causes first degree burns to the skin in short-time exposure.	Federal Standard 313B
Corrosive material	Any solid, liquid, or gaseous substance that burns, irritates, or destroys organic materials, most notably the skin, and when taken internally, the lungs and stomach.	NFPA
Corrosive liquid	Has a severe corrosion rate that exceeds 6.35 mm (0.250 in.) per year on steel (SAE 1020).	DOT 49CFR173.240
Corrosive material	A liquid or solid that causes visible destruction or irreversible alterations in human skin tissue at the site of contact. In case of a leak, a liquid that has a severe corrosion rate on steel.	DOT 49CFR173.240
Corrosivity	Aqueous solution has a pH less than or equal to 2 or greater than or equal to 12.5. A liquid that corrodes steel (SAE 1020) at a rate greater than 6.35 mm (0.250 in.) per year at 55°C.	EPA 40CFR261.22
Corrosive	Any substance that when in contact with CPSC 16CFR1500.3 living tissue causes destruction of the tissue by chemical action, but shall not refer to action on inanimate surfaces.	
Corrosive Chemical	A chemical that on contact with living tissue causes destruction of the tissue by chemical action., This term shall not refer to action on inanimate surfaces.	ANSI 2129.1

All 12 categories were subjected to such review, which led to 57 subcategories of hazardous materials. These materials are shown in Table 2 with their appropriate categories.

In addition to the 13 subcategories identified under Multiple Hazard Materials, DOT also presented the priority list of materials for multiple hazard not previously listed (Table 3). These priorities identify which hazard grouping will take precedence for hazard identification for storage criteria. For example, a material defined as both an irritating material and an oxidizer, will be classified as an oxidizer.

To follow through on our corrosive materials group, the definitions for the four subcategories of corrosives are found in Table 4.

TABLE 2—*Hazardous materials subcategories.*

Hazardous Material	Subcategories
1. Flammables	flammable liquid, Class IA
	flammable liquid, Class IB
	flammable liquid, Class IC
	combustible liquid, Class II
	combustible liquid, Class IIIA
	combustible liquid, Class IIIB
	flammable solid
	spontaneously combustible solid
	dangerous when wet solid
2. Corrosives	acidic liquid
	alkaline liquid
	acidic solid
	alkaline solid
3. Oxidizers	oxidizer
4. Compressed gases	flammable gas
	poison gas
	nonflammable gas
5. Radioactive materials	radioactive White-I
	radioactive Yellow-II
	radioactive Yellow-III
	radioactive, license exempt
6. Poisonous/Infectious Substances	poisonous liquid, Class A
	poisonous liquid, Class B
	poisonous solid, Class B
	irritant
	etiologic agent
7. Organic Peroxides	organic peroxide
8. Explosives	explosive Class A
	explosive Class B
	explosive Class C
	blasting agents
9. Pesticides	pesticides, Category I
	pesticides, Category II
	pesticides, Category III
	pesticides, Category IV
10. Other regulated materials (ORMs)	ORM-A
	ORM-B
	ORM-C
	ORM-D
	ORM-E
11. Personnel hazard communication group materials	eye
	respiratory
	skin
	ingestion
12. Multiple hazard materials	radioactive and any other hazard
	explosive and any other hazard
	Poison A and any other hazard
	oxidizer and Poison B
	flammable solid and Poison B
	flammable liquid and Poison B
	flammable solid and water reactive
	corrosive and Poison B
	Poison B and corrosive
	Poison B and flammable liquid

TABLE 2—*Hazardous materials subcategories.*

Hazardous Material	Subcategories
12. Multiple hazard materials (continued)	flammable liquid and corrosive flammable solid and corrosive oxidizer and corrosive

TABLE 3—*Priority of hazard for multiple hazard materials.*

1. Radioactive materials
2. Poison A
3. Flammable gas
4. Nonflammable gas
5. Flammable liquid
6. Oxidizer
7. Flammable solid
8. Corrosive liquid
9. Poison B
10. Corrosive solid
11. Irritant materials
12. Combustible liquid (in containers of more than 110 gal [416 L])
13. ORM-B
14. ORM-A
15. Combustible liquid (in containers less than 110 gal [416 L])
16. ORM-E
17. ORM-C

TABLE 4—*Corrosives.*

Subcategory	Definition
Corrosive liquid, acidic	A liquid, other than a general pesticide, with a pH of less than 6, which causes visible destruction or irreversible alterations in human tissue at the site of contact, or a liquid that has a severe corrosion rate on steel, as defined in 49 CFR 173.240.
Corrosive liquid, alkaline	A liquid, other than a general pesticide, with a pH of more than 8, which causes visible destruction or irreversible alterations in human tissue at the site of contact or a liquid that has a severe corrosion rate on steel, as defined in 49 CFR 173.240.
Corrosive solid, acidic	A solid that yields a solution pH of less than 6 and causes visible destruction or irreversible alterations in human tissue at the site of contact, in accordance with test methods prescribed in Appendix A of 49 CFR 173.
Corrosive solid, alkaline	A solid that yields a solution pH of more than 8 and causes visible destruction or irreversible alterations in human tissue at the site of contact, in accordance with test methods prescribed in Appendix A of 49 CFR 173.

Finalization of Subcategories

Once the 57 subcategories were properly identified, it became apparent that there was still not sufficient refinement in definitions to effect compatible and cost efficient storage. Although the definitions of some subcategories were quite specific and could be stored as is, others could not. For this reason, certain subcategories had to be more explicitly defined relative to their physical and chemical characteristics and storage requirements. Figures 1 through 11 illustrate the evolution of the 12 original categories into the 77 final haz-

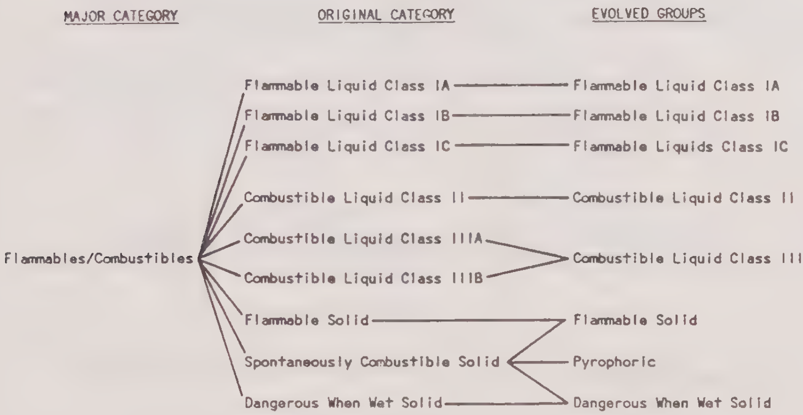

FIG. 1—*Evolution of HSCG's, flammables/combustibles.*

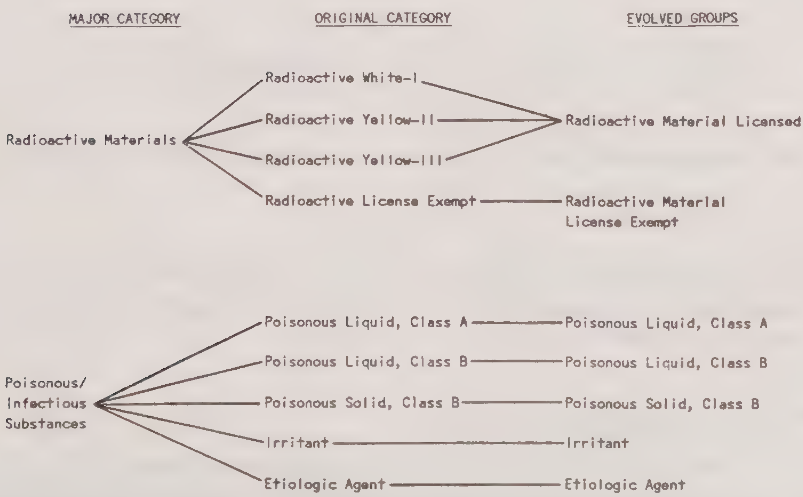

FIG. 2—*Evolution of HSCG's, radioactive materials and poisonous/infectious substances.*

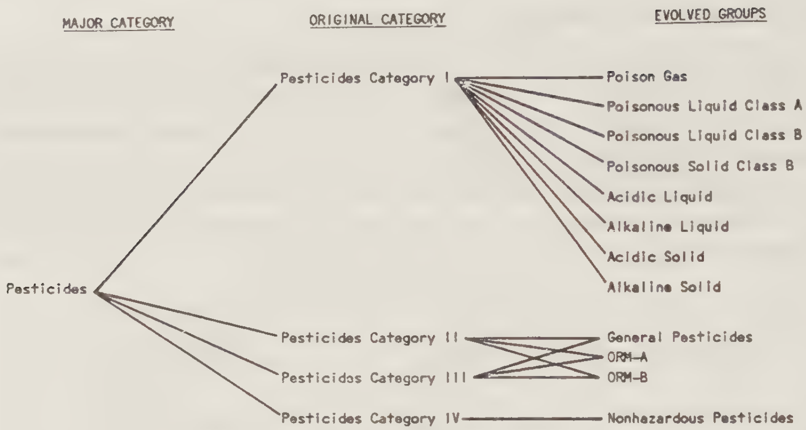

FIG. 3—*Evolution of HSCG's pesticides.*

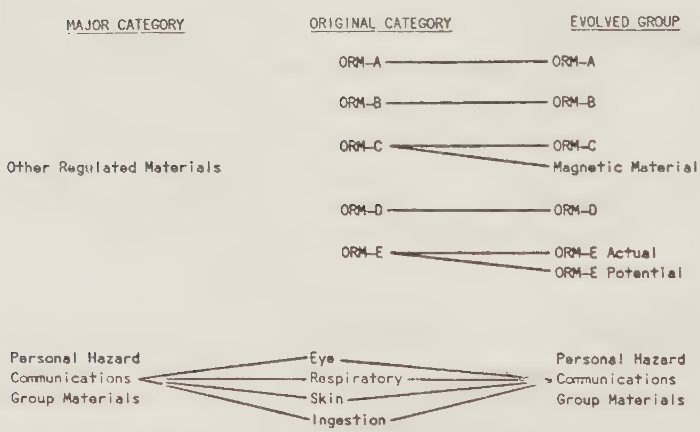

FIG. 4—*Evolution of HSCG's, ORM and personal hazard communication group materials.*

ardous storage compatibility groups (HSCG's). Justification for expansion, recombination, or elimination of the intermediate 57 subcategories or all of the above is provided as follows.

Flammable/Combustible Liquids

Flammable/combustible liquids are classed according to their flash points and boiling points. The flash points of Class IIIA and IIIB liquids, 60°C (140°F) and above, are sufficiently high so as not to present a storage hazard

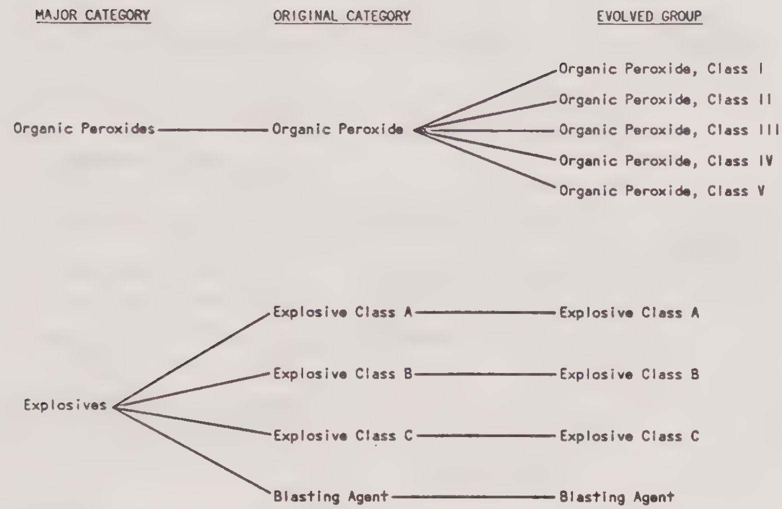

FIG. 5—*Evolution of HSCG's, organic peroxides and explosives.*

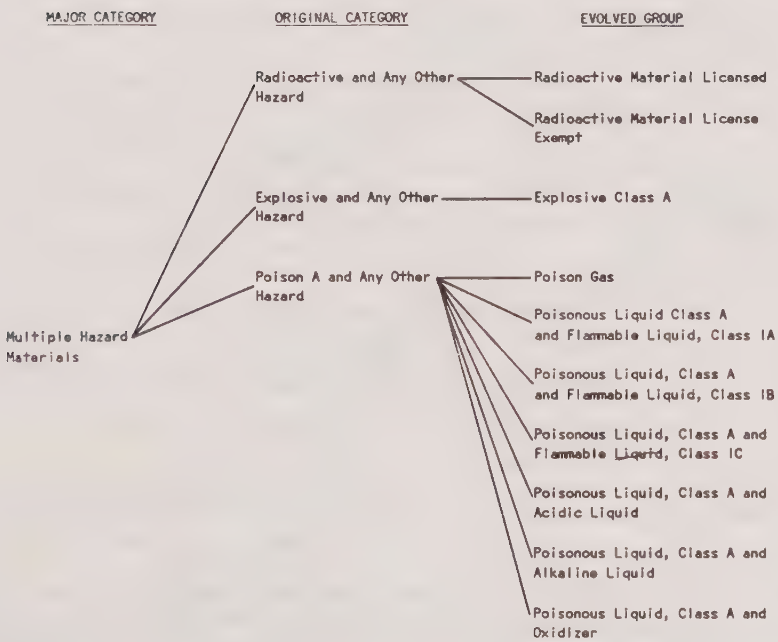

FIG. 6—*Evolution of HSCG's, multiple hazard materials—radioactive, explosive, and Poison A materials.*

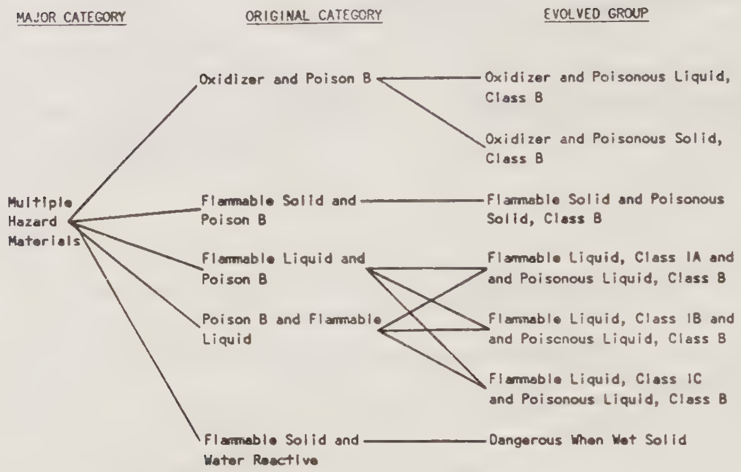

FIG. 7—*Evolution of HSCG's, multiple hazard materials—oxidizers, flammables, and Poison Bs.*

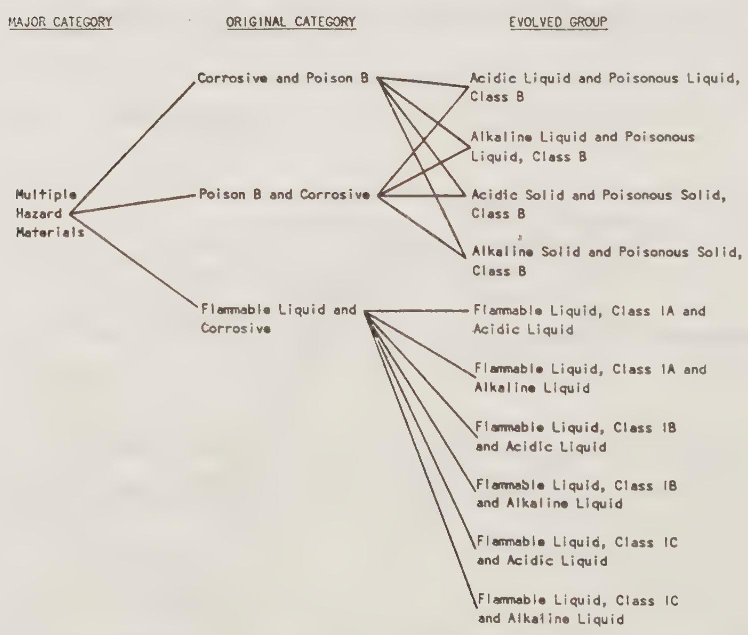

FIG. 8—*Evolution of HSCG's, multiple hazard materials—corrosives, Poison Bs, and flammables.*

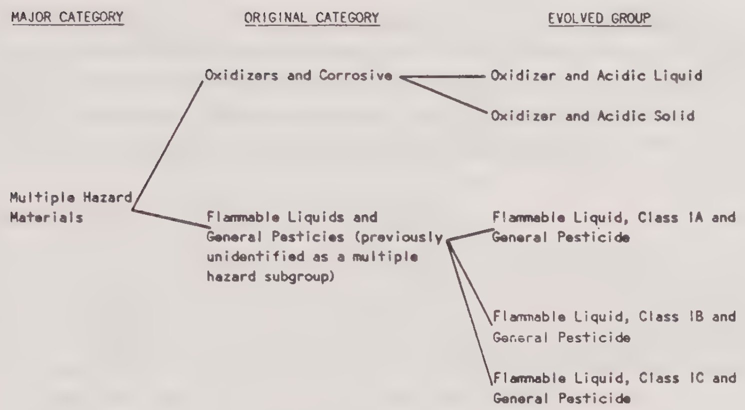

FIG. 9—*Evolution of HSCG's, multiple hazard materials—oxidizers and corrosives; flammable liquids and general pesticides.*

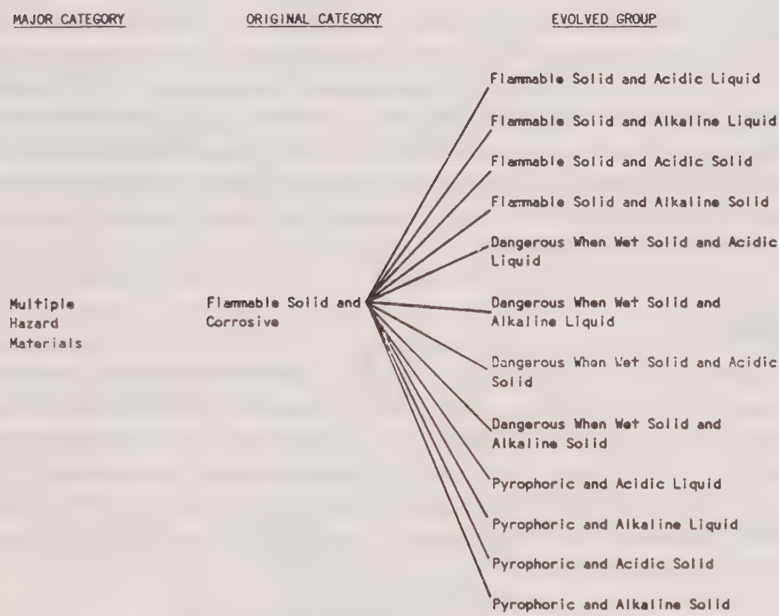

FIG. 10—*Evolution of HSCG's, multiple hazard materials—flammable solids and corrosives.*

under normal warehouse conditions. Because DOT, OSHA, and NFPA view Class IIIA liquids as minimally hazardous and do not recognize a hazard with Class IIIB liquids, both Class IIIA and IIIB liquids are combined into one storage category (Fig. 1).

The flammable/combustible solids category includes subcategories identi-

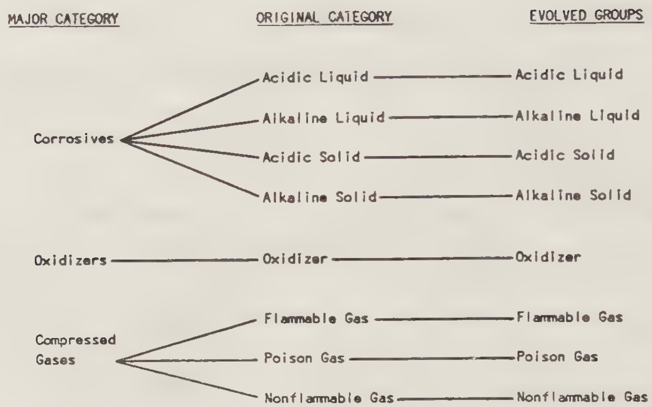

FIG. 11—*Evolution of HSCG's, multiple hazard materials—corrosives, oxidizers, and compressed gases.*

fied as flammable solid, spontaneously combustible, and dangerous when wet. Depending on the agency or organization that defines the subcategory, the three member subcategories may be separately unique, or identified as a subcategory of another. In either case, these subcategories were not distinct enough in their regulatory definitions to be stored as is. A fourth subcategory, pyrophoric, was resident in each of the other three definitions and presented a very serious threat to safe storage.

Pyrophorics

A substantial ignition source, pyrophorics could not be stored with known fuel sources such as flammable solids. As a result, pyrophoric was deleted from the definition of spontaneously combustible and given separate storage status. The remainder of the materials associated with spontaneously combustible fell neatly into flammable solid and dangerous when wet (Fig. 1). Thus the subcategory of spontaneously combustible was eliminated and replaced by pyrophoric.

Radioactive Material

Radioactive material is most easily recognized in its packaged state by the presence of the White I, Yellow II, or Yellow III DOT label. However, the choice of label is more a function of packaging than the hazard associated with the isotope within. The application of a label on a packaged product indicates the presence of a radiation hazard in the basic unit of issue significant enough to warrant segregated storage with Fig. 1 monitoring. Therefore,

all radioactive materials requiring a label on the basic unit of issue were grouped together as radioactive material licensed. The absence of a label on the basic unit of issue indicates that (1) no hazard exists, or (2) the hazard is negligible. Therefore, all radioactive material not requiring a label on the basic unit of issue was left as a separate subgroup (Fig. 2).

Poisonous/Infectious Substances and Pesticides

The following diagram (Fig. 12) illustrates a comparison of EPA/FIFRA Category I pesticides and the DOT Classes of Poison A, Poison B, and corrosive. The specific criteria of LD_{50} and corrosivity utilized by EPA/FIFRA is similar enough to the more broad criteria of DOT to effectively place any EPA/FIFRA Category I pesticide into one of three DOT classes.

EPA/FIFRA Category I pesticides are also identified by name in 49 CFR 172.101 as Poison A material. At present, all Poison A materials, according to DOT, are gases.

EPA/FIFRA Category I pesticides meet the definition of a DOT Poison B. These pesticides will be included in the DOT designation. Poison B materials are further subdivided into liquids and solids. These same criteria will apply to EPA/FIFRA pesticides.

EPA/FIFRA Category I pesticides are evaluated not by toxicity data but by their corrosive effects on the eyes and skin. The corrosivity criteria for eyes and skin utilized by EPA/FIFRA are identical to those utilized by DOT to evaluate corrosives.

EPA/FIFRA Categories II, III, and IV may be regulated by DOT as ORM-A or ORM-D class material. If the pesticide uses a flammable or combustible solvent, these materials will be regulated for their flammability only.

In summary, EPA/FIFRA Category I pesticides were absorbed into either poison gas, poison liquid A, poison liquid or solid B or one of the four corro-

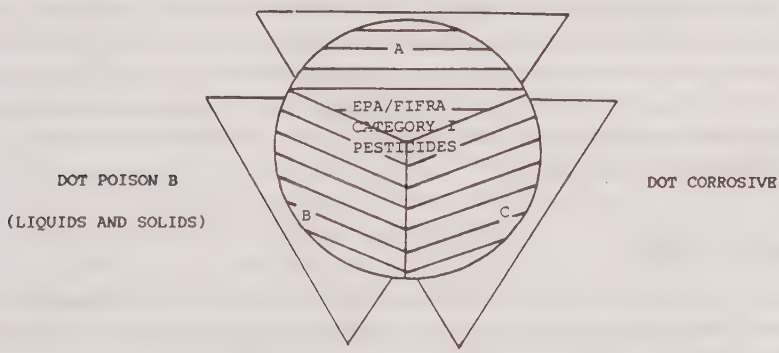

FIG. 12—*DOT Poison A (liquid or gas).*

sive subcategories. EPA/FIFRA Category II, III, and IV were absorbed into either ORM-A, ORM-D, or became general pesticides. Pesticide Category IV became nonhazardous pesticides (Fig. 3).

ORM

The recognized definition of ORM-C as established by DOT includes magnetic material along with other materials such as inflatable rafts, burlap bags, battery parts, and bleaching powder. To prevent the storage of magnetized items adjacent to items that may be sensitive to magnetism, magnetic materials were individually extracted from all other ORM-C items and given separate storage status. In addition, DOT requires the application of a distinct magnetic label to all items meeting their criteria when shipped by air. Such is not the case with other nonmagnetic ORM-C material.

The separation of ORM-E material into two groups was necessary to identify those items that, as a result of packaging and content, meet the definition of reportable quantity material and those that have the potential for becoming reportable quantity material as more than one package is normally stored in a warehouse. ORM-E material that meets the reportable quantity criteria must be sorted in secure monitored facilities. Those materials that have the potential of becoming reportable quantity criteria must be sorted in secure monitored facilities. Those materials that have the potential for becoming reportable quantity material do not as yet pose a hazard and are therefore given a status separate from the actual ORM-E. When dealing with ORM-E (potential), caution must be exercised to monitor large accumulations of this material in centralized warehouse locations (Fig. 4).

Personal Hazard Communications Group

The Personal Hazard Communications Group was recombined because the routes of entry (that is, eye, respiratory, skin, and ingestion) were insignificant compared to the overall hazard. The hazard is that of a nuisance. If the material can truly cause damage via a route of entry, it will have been previously identified with another of the major groups with regard to storage concerns. This category provides for the identification of nonhazardous dusts and powders, glue, stain, odoriferous substances, and the like that are not categorized elsewhere (Fig. 4).

Organic Peroxides

According to 49 CFR 173.151a(a), any organic compound that contains the bivalent o-o structure and that may be considered a derivative of hydrogen peroxide where one or more of the hydrogen atoms has been replaced by organic radicals must be classed as an organic peroxide unless one or more of four exceptions applies.

Within the scope of this broad definition are many compounds that present drastically varied reactivities. These reactivities range from violent deflagration to relatively no reactivity. Because of the variations in reactivity and in the storage environments necessary to control reactivity, this document addresses organic peroxides as five distinct groups of material. Organic peroxide Class I includes those compounds considered most reactive, and organic peroxides Class V include those compounds considered nonreactive or with little reactivity (Fig. 5). It is incumbent upon manufacturers or producers to properly classify their respective organic peroxide compounds.

The use of this organic peroxide classification scheme is currently being evaluated by industry. To date, little qualitative or quantitative work has been done to properly define and categorize organic peroxides.

Multiple Hazard Materials

As previously stated, only DOT had developed specific combinations of single hazards for which multiple hazard warning requirements could be applied. In addition, DOT provided guidance as to how to properly classify multiple hazard materials. The difficulty in applying DOT criteria is in ensuring that all materials that are to be classified can be related to their definitions.

After careful development and review of all single hazards presented in this document, the next task was to identify specific combinations of any two single hazards that might be realistically encountered in a storage environment. All single hazards were compared to each other and the combinations evaluated based on two questions: (1) did the combination represent a multiple hazard or was it still a single hazard as with flammable liquid compared to flammable or corrosive liquid, acid compared to corrosive and (2) was the combination chemically feasible and realistic? An example of the second situation is the combination of corrosive liquid, alkaline, and corrosive solid, alkaline and oxidizer.

The combinations that actually represented a multiple hazard and were chemically feasible were identified as groups and given separate storage status (Figs. 6 through 10).

In evaluating combinations with radioactive licensed material, it was determined that the stringent radioactive packaging requirements would practically eliminate the need for specifically identifying any radioactive licensed material as a multiple hazard. This same philosophy was applied to Explosives A, B, C, and blasting agents, which were pooled in a single subcategory when combined with any other hazard (Fig. 6).

The primary reasons for the expansion of the multiple hazard combinations as developed by DOT were (1) the expansion of the single, corrosive category into poison subgroups of liquids, solids, acids, and alkalines, (2) poison Class A was expanded to include both gases and liquids, and (3) poison Class B was expanded to identify both liquids and solids. In addition. the

generation of the single hazard, general pesticide, accounted for one multiple hazard, that being flammable and general pesticide (Fig. 9).

DOT recognized one large division of flammable solids that this document treats as three: flammable solids, dangerous when wet, and pyrophorics. This subdivision led to new groups (Fig. 10).

In one instance DOT repeated the combination of corrosive and poison, Class B. These duplicative combinations were combined; however, this resulted in four groups as corrosive subdivided into acids, alkalines, liquids, and solids (Fig. 8).

No changes were made to the groups contained in the major categories of corrosives, oxidizers, and compressed gases (Fig. 11), when not combined with other hazards.

Figures 1 through 11, Evolution of Hazardous Storage Compatibility Groups, gives pictorial presentation of the evolution from 57 subcategories to 77 HSCG's.

Summary

In summary, we have reviewed all pertinent definitions of hazardous material, identified 12 major categories of hazardous materials, subdivided those 12 groups into 57 subcategories based on the regulatory definitions, and evolved those 57 subcategories into 77 hazard storage compatibility groups by resolving differences, overlaps, and duplications. Next we are going to look at storage requirements for each of the 77 HSCG's, evaluate chemical characteristics as pertains to the storage environment, and develop a storage compatibility guide. Following that, specific storage procedures will be developed for each HSCG.

Summary

As discussed in the Introduction, this book is the sixth ASTM Special Technical Publication (STP) on the subject of new test methods to assess and control the handling of hazardous and industrial solid wastes. Sound testing methods are needed to complement the range of engineering practices being developed in the solid waste management area.

Contaminant and Leaching Assessment

Tests of wastes are required to predict the tendency of toxic constituents to leach. Results are used to guide the selection of safe disposal practices.

Philipp, Endell, Raguin, and Dechelette describe an eight-laboratory study under the auspices of the International Iron and Steel Institute that compared the results of standard leaching tests of nine countries with two types of slag, one sludge and three dusts. One interesting finding was that lead extracted from blast furnace slag by the U.S. Environmental Protection Agency (EPA) test was over 50 times in excess of the standard, whereas it was more than 100 times below the standard imposed for the French and Japanese tests.

Ham, Boyle, and Blaha compare laboratory leach tests of foundry wastes with actual landfill leachate quality. The U.S. EPA acetic acid leaching procedure was marginally more useful than a similar procedure using deionized water in predicting the presence or absence of problem constituents in landfill leachate; neither was able to predict accurately parameter concentrations. Leach tests on auger samples of buried wastes were more accurate than leach tests on raw wastes.

Pilot-scale leaching tests developed by Pohland and Gould showed that heavy metal sludge could be assimilated within a landfill when it is disposed with municipal refuse down to a ratio of 1 : 13 and exposed to the influence of leachate containment and recycle.

Instead of applying a standard leach test with its one set of environmental conditions to a waste, Cote, Briddle, and Benedek surveyed and described the intrinsic properties of a solidified waste that relates to leachability under any set of environmental conditions.

Brown, Bishop, and Gress used up-flow column leaching tests to study the release patterns of heavy metals from stabilized/solidified heavy metal sludges. Particle size was found to be important, primarily because of the loss of alkalinity, which allowed metal release.

The selection/specification of parameters to reduce variability in the ASTM batch leach tests is presented by Jackson. The ASTM column leach test is described by Miner, Maltby, and Dell.

Ground-Water and Contaminant Migration Assessments

Chemical interaction and advection/diffusion modeling of leachate constituents from a landfill overlying clay are described by Quigley and Rowe (Canada). DeVille and Malloy developed a management system for handling ground-water monitoring data with emphasis on error checks and quality assurance.

The effect of pH and soil organic carbon content on adsorption of pentachlorophenol is described by Banerji, Piontek, and O'Connor; 84% of the adsorption was reversible. The rate and extent of adsorption of mixed dichlorobenzene and dichlorophenol was determined by Uchrin and Katz; the two-solute system showed enhanced adsorption by some soils.

Design and operating factors that affect bioreclamation of ground water at the surface and *in situ* are identified and discussed by Parkin and Calabria; means are described to select proper environmental conditions and to provide adequate contact between the bacteria and the contaminants.

ASTM guides for sampling ground-water monitoring wells and for pore water sampling in the Vadose Zone are described by Bone and Morrison. Sampling devices, flushing procedures, and sample preservation are emphasized.

Incineration of Hazardous Waste

Performance assessments of thermal systems for destroying hazardous waste are described by Oppelt. Parameters monitored are SO_x, NO_x, particulates, hydrochloric acid (HCl), carbon monoxide (CO), carbon dioxide (CO_2), oxide (O_2), metals, total hydrocarbons, and specific organic compounds of concern; these are related to process operating variables. Particulate emissions turned out to be the most difficult standard to attain for incinerators.

Liner Assessments

An overview of the manufacturing, properties, installation, and compatibility testing of flexible membrane liners is presented by *Koerner*. Improved accelerated aging tests, field seam test methods, and leak location methods are needed.

The use of *in-situ* soil as part of a clay liner was studied by Yong, Warith, and Boonsinsuk; heavy metals tended to be significantly attenuated most likely through coprecipitation and fixation. The effect of pore fluid pH on the dynamic shear modulus of clay-sand mixture was described by Du,

Mikroudis, and Fang, for acidic fluids the modulus of the kaolinite samples increased as the pH decreased, the opposite was the case for bentonite.

Site Monitoring and Assessment

An array of remote methods for assessing waste sites is described by Wruble, van Ee, and McMillion. These are classified as airborne, ground surface, and subsurface or down hole. Airborne techniques include infrared photography and multispectral scanning. Surface methods are seismology, magnetometry, ground-penetrating radar, resistivity, and electromagnetic induction. Subsurface approaches include induction logging, gamma profiles, and optical fibers tipped with optrodes for laser-induced fluorescence detection of contaminants.

ASTM guidelines for sampling solid wastes from point sources and impoundments are described by Holcombe, Johnson, and Lorenzen; methods for determining the required number of samples are included.

A single probe that combines the functions of a tensiometer and a lysimeter is applied in an ASTM method by Morrison and Mioduszewski for use in monitoring leaks from underground storage tanks and impoundments.

Waste Testing

The analysis of waste with complex chemical matrices is described by Rohlik. In this paper he discusses separation and preparation of samples, implications of oxidation and reduction, adaptation of simple matrix methods and the use of modeling, waste background information and process analytical tools in solving the complex chemical matrix problem.

Katz and Jennis reviewed and evaluated procedures being used for the determination of micro-nutrients, macro-nutrients, and some toxic elements in sewage sludge. Inductively coupled plasma spectroscopy (ICPS) analysis seems to be an extremely useful analytical tool considering speed, sensitivity, and selectivity.

Waste Treatment Alternatives

Cement-based grouts were used by Gilliam, Dole, and McDaniel for the immobilization for four simulated waste streams. Grout formulations were compared and leach tests were performed. All wastes, including the organics were suited for this type of treatment. Tittlebaum, Eaton, Cartledge, Walsh, and Chalasani employed the use of scanning electron microscopy, energy dispersive X-ray analysis, electron probe analysis, and X-ray powder diffraction to study cement-based solidified/stabilized wastes. The use of these short-term testing techniques when combined properly provide a method for identi-

fying mechanisms of waste stabilization. They were found particularly useful for evaluating the solidification of organics.

Biological treatment of toxic or inhibitory wastes were reviewed and collated by Rozich and Gaudy. The use of standard aerobic treatment processes were evaluated in light of the inhibitory nature of toxic wastes and were found to be easily adapted to the treatment of these wastes.

ASTM Test Method Development

Some of the work of Committee D-34 on Waste Disposal was presented at a one-day symposium in Colorado Springs, CO, before the international symposium in Alexandria, and is contained in this STP.

Bone discusses standards that have been developed for sampling ground-water monitoring wells and for the analysis of ground water. The procedures for sampling ground-water monitoring wells assumes that the wells have been properly installed and developed, and the analysis of ground water is limited to evaluation of EPA's Method 8600 proposed in EPA Manual SW-846. Soil moisture monitoring and techniques for sampling of pore water in the vadose zone are given a comprehensive and detailed review by Morrison and Mioduszewski. Application of these techniques to underground storage tanks and surface impoundments are described.

Guidance for collecting representative samples of wastes from point discharges and impoundments is described by Holcombe, Johnson, and Lorenzen. Safety procedures, design considerations, equipment, and sampling procedures are outlined.

Jackson describes the history and development of the first standard leaching test for solid waste. Comparisons with the EPA Toxic Extraction Procedure were also made. Another group in ASTM is attempting to develop a column leaching method for solid waste. This group's efforts are presented by Miner, Maltby, and Dell.

The development of a standard test for comparing the adsorption properties of various soil materials is described by Griffin, Sack, Roy, Ainsworth, and Krapac. The test presents an initial and a 24-h solution concentration as a distribution ratio between solutes and soil materials. This method should prove particularly useful to consultants and regulators alike in assessing attenuation potential of soils.

Rinaldo-Lee evaluated the use of a paint filter test proposed by EPA to determine the free liquid content of waste. Six laboratories participated in the testing of four different waste samples as part of this study. Two major problems were identified concerning the usefulness of this test: (1) separation of the mesh from the cardboard filter holder and (2) differences in filter design.

Although generally small in quantity, chemical laboratories generate a large number of diverse waste streams. McKee describes the committee's

work on the development of a currently improved guide for the disposal and handling of laboratory chemicals and samples.

Warner, Frick, Lovejoy, and Burns present a new classification scheme to facilitate the storage of hazardous materials and waste. Seventy-seven hazard storage compatibility groups were identified for which specific storage requirements are to be developed.

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The Roman numerals printed in boldface type refer to the particular symposium in the series of solid waste testing symposia. The First Symposium (**I**) is reported in STP 760,[1] **II** in STP 805,[2] **III** in STP 851,[3] **IV** in STP 886,[4] **V** in STP 925,[5] and **VI** in STP 933.[6]

Subject Index

[1] *Hazardous Solid Waste Testing: First Conference, ASTM STP 760,* R. A. Conway and B. C. Malloy, Eds., American Society for Testing and Materials, Philadelphia, 1981.

[2] *Hazardous and Industrial Solid Waste Testing: Second Symposium, ASTM STP 805,* R. A. Conway and W. P. Gulledge, Eds., American Society for Testing and Materials, Philadelphia, 1983.

[3] *Hazardous and Industrial Waste Management and Testing: Third Symposium, ASTM STP 851,* L. P. Jackson, A. R. Rohlik, and R. A. Conway, Eds., American Society for Testing and Materials, Philadelphia, 1984.

[4] *Hazardous and Industrial Solid Waste Testing: Fourth Symposium, ASTM STP 886,* J. K. Petros, W. J. Lacy, and R. A. Conway, Eds., American Society for Testing and Materials, Philadelphia, 1985.

[5] *Quality Control in Remedial Site Investigation: Hazardous and Industrial Waste Testing, Fifth Volume, ASTM STP 925,* C. L. Perket, Ed., American Society for Testing and Materials, Philadelphia, 1986.

[6] *Hazardous and Industrial Solid Waste Testing: Sixth Volume, ASTM STP 933,* D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Lacy, Eds., American Society for Testing and Materials, Philadelphia, 1986.

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